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THERMALLY STABLE

PERFLUORINATED POLYMERS

Henry C. Brown

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Air Force Materials Laboratory
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Wright-Patterson Air Force Base, Ohio

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NOTICES

FOREWORD

This report was prepared by the University of
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Engineer.

This report covers work which was performed
during the period March 1, 1965 through February 28, 1966,
under the direction of Dr. Henry C. Brown, Principal Investigator.
Other personnel employed during this period included
Mr. Gerald McNeely, Mr. H. J. Gisler, Mr. John Ernsberger, and
Mr. D. M. Chauncey, Research Assistants.

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approved.

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Chief, Polymer Branch
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ABSTRACT

Work on the poly(perfluoroalkylene-1,2,4,4$\underline{H}$-triazole system has been continued with the objectives of increasing the polymer molecular weights, inactivating the polymer chain end-groups and studying polymer chemical and physical properties. A new synthesis of an intermediate polymer structure for this system has been found which involves addition of perfluoroalkyl-dihydrazides to perfluoroalkyldinitriles in a highly polar solvent. Inactivation of end-groups has been possible by conversion to -CF$_2$COOH with subsequent decarboxylation to -CF$_2$H.

Methods of synthesis of poly(perfluoroalkylene-1,3,4-oxadiazoles) that have been studied include the direct formation of the oxadiazole ring by acylation of a bis(tetrazolyl) perfluoroalkane and formation of an intermediate poly(perfluoro-diacyl hydrazine) from the reaction of perfluorodiacyl chlorides with perfluoroalkyldihydrazides.

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I. INTRODUCTION

The objective of this research is the synthesis and study of high molecular weight polymeric materials that are stable at high temperatures and are chemically inert. Perfluoroalkyl-substituted heterocyclic compounds have been shown to have high thermal stability, and it is the particular purpose of this research to find methods of incorporating these units into polymer structures, preferably of the type in which nitrogen, oxygen or sulfur-containing heterocycles are connected by perfluoroalkylene chains.

During the present contract period the work on this project has been devoted principally to the study of the poly(perfluoroalkylene-1,2,4,4H-triazole) and the poly(perfluoro-alkylene-1,3,4-oxadiazole) systems. The objective of the work on the triazole system was to increase the molecular weight, inactivate the polymer chain end-groups and study the properties of this polymer chain with its strongly acidic heterocyclic groups. A new polymerization reaction, in which a perfluoroalkyl dihydrazide adds to a perfluoroalkyl dinitrile in the presence of a basic solvent, was found and promises to furnish a route to a higher molecular weight intermediate structure for triazole polymers than the previously used methods of synthesis. Inactivation of end-groups has been accomplished by hydrolysis and subsequent decarboxylation. Studies of the properties of the poly(perfluoroalkylene-1,2,4,4H-triazoles) is continuing.

Methods of synthesis of the poly(perfluoroalkylene-1,3,4-oxadiazole) have included the formation of the oxadiazole ring directly from the reaction of a perfluorodiacyl chloride with 1,3-bis(5-tetrazolyl)perfluoropropane and the formation of an intermediate poly(perfluoroalkylene-1,2-diacylhydrazine) from the reaction of a perfluoroalkyl dihydrazide with a perfluorodiacyl chloride. This latter polymer structure has not yet been cyclized to the oxadiazole structure.

II. DISCUSSION

A. Poly(perfluoroalkylene-1,2,4,4H-triazoles)

1. Further reactions of the cyclic monomer, 1,2-diaza-3-imino-7-amino-4,4,5,5,6,6-hexafluorocycloheptene-7

The initial work with the cyclic monomer 1,2-diaza-3-imino-7-amino-4,4,5,5,6,6-hexafluoro-7-cycloheptene, I, was described in the previous technical report.[1] During the

$$\begin{array}{c} \text{N-NH} \\ \text{H}_2\text{N-C} \qquad \text{C=NH} \\ | \qquad\qquad | \\ \text{F}_2\text{C} \qquad\qquad \text{CF}_2 \\ \text{CF}_2 \end{array} \qquad \text{I}$$
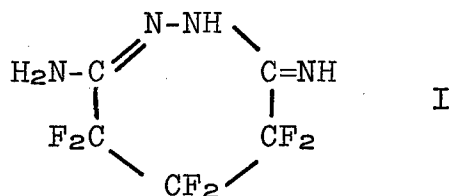
present period this monomer was treated with hydrogen chloride at a higher temperature for a longer period of time than was previously reported. The polytriazole obtained was subjected to further heating under reduced pressure at 225° for 8 hr. to remove the ammonium chloride formed. About 15% of the polymer prepared by this procedure was insoluble in tetrahydrofuran. The tetrahydrofuran soluble portion of the polytriazole was heated under reduced pressure at 375° for 8 hr. and became insoluble in tetrahydrofuran. This material was placed in 10% sodium hydroxide solution, and after two weeks, about 30% had dissolved; the base-soluble portion was recovered by acidification and was found to be insoluble in tetrahydrofuran. The infrared spectra of the base-soluble polymer indicated that it retain the triazole structure. A suitable solvent for determination of the molecular weight of the tetrahydrofuran-insoluble polymer has not yet been found.

Additional attempts were made to carry out the polymerization using the cyclic monomer I with various solvent and dehydration agents. The polytriazole structure was not obtained under the following conditions: (1) polyphosphoric acid at 175° for 12 hr; (2) acetic acid in bis(2-ethoxyethyl) ether at 110° for 40 hr. and at 150° for 86 hr.; (3) in diglyme and acetic acid at 115° for 48 hr. and at 135° for 90 hr.; (4) in methyl carbitol with acetic acid at 90° for 12 hr. and at 140° for 5 days.

2. Polymers of the type $-\left[R_F C(=O)NHNHC)=NH) \right]_n$ and their conversion to polytriazoles

a. Acylation of perfluoroacylhydrazidines

An alternative method for producing a poly(perfluoroalkylene-1,2,4-triazole), other than the addition of hydrazidines to nitriles or the use of the cyclic monomer I, involves the

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reaction of a perfluoroacylchloride with a perfluoroalkyl-
hydrazidine as shown in Eq. 1.

$$(CF_2)_3 \left(\begin{array}{c} NH_2 \\ C \\ \parallel \\ N\text{-}NH_2 \end{array} \right)_2 + (CF_2)_3 \left(\begin{array}{c} O \\ C \diagup \\ \diagdown Cl \end{array} \right)_2 \xrightarrow{-HCl} \left[\begin{array}{cc} NH_2 & OH \\ \mid & \mid \\ C & C\text{-}(CF_2)_3 \\ \parallel & \parallel \\ N\text{-}N \end{array} \right]_n$$

A

$$\Bigg\downarrow {-H_2O}$$

$$\left[\begin{array}{cc} & NH \\ & \diagup \quad \diagdown \\ C & \quad C\text{-}(CF_2)_3 \\ \parallel & \parallel \\ N\text{-}N \end{array} \right]_n$$

B

Eq. 1
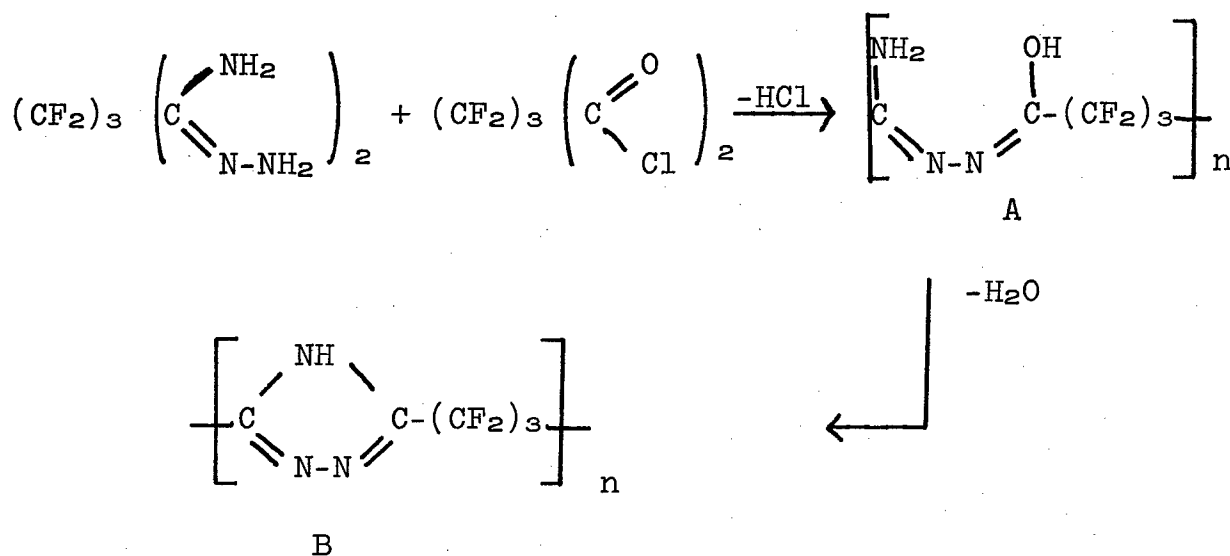
The initial acylation reaction should produce a linear inter-
mediate A, which on loss of water would give the triazole
polymer shown at B. The linear intermediate, A, would also
be an interesting one to work with due to the possibility of
ring closure by loss of ammonia (to give the oxadiazole ring)
or by loss of water to give the triazole ring. With an inter-
mediate polymer of this type, in a high molecular weight, it
might be possible to adjust the dehydration or the deammona-
tion condition so that selected members of each type of hetero-
cyclic ring were produced along the polymer chain.

Two difficulties are immediately apparent in the
reaction sequence shown in Eq. 1. The first is that hydrogen
chloride, evolved during the acylation, may react with the
hydrazidine to form a hydrochloride salt and hinder the further
reaction of the perfluoroacylchloride. The second difficulty
is that water may be evolved from the immediate linear polymer
and hydrolyze the remaining perfluoroacylchloride before the
desired acylation reaction is completed.

In the previous report[1] the reaction between perfluoro-
butyrhydrazidine hydrochloride and perfluoropropionyl chloride
was discussed. In this reaction it was determined that the
acyl chloride would react with the hydrazidine hydrochloride
and the product obtained was 3-perfluoropropyl-5-perfluoroethyl-
1,2,4-triazole. In this reaction the perfluoropropionyl chloride
apparently acted as a dehydrating agent and closed the ring with
elimination of water.

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During the present period this type of reaction was repeated using perfluorobutyrhydrazidine hydrochloride and perfluorobutyryl chloride at a lower temperature in attempt to isolate the acylated hydrazidine. The reaction was carried out in a sealed tube at 70° and the product obtained was a white solid. Infrared spectra of this solid material indicated that it was a mixture of the diacylated hydrazine and a perfluoropropyl-substituted triazole. Attempts to separate these two compounds by recrystallization, sublimation, and acidification of the mixture were unsuccessful. These two products may have resulted from the splitting out of water from the linear intermediate to give the triazole and this water could have reacted with additional intermediate product to give the diacylhydrazine. In this reaction, unlike the one described previously, there was no excess acyl chloride present.

This type of acylation reaction was extended to perfluoroglutarhydrazidine and perfluorobutyrylchloride. Attempts to prepare perfluoroglutarhydrazidine hydrochloride indicated that the compound was not very stable and, therefore, the reaction between the hydrazidine and the acid chloride should proceed with less interference from formation of the hydrochloride salt. The initial reaction was carried out by sealing perfluoroglutarhydrazidine and an excess of perfluorobutyryl chloride in a glass tube and heating at 50° with the hope that this temperature, lower than that previously used for the acylation reactions, would prevent splitting out of water and allow the separation of the diacylated glutarhydrazidine. However, the product obtained was a dark tacky material whose infrared spectra indicated that it contained the imidoylhydrazidine structure rather than the acylated structure.

Perfluoroglutarhydrazidine was successfully acylated with perfluorobutyryl chloride by adding the acid chloride to carbon tetrachloride solution of the hydrazidine to which had been added triethylamine as a hydrogen chloride acceptor. This reaction was carried out at 5°. The resulting reaction mixture was a slurry which was filtered and the solid separated was washed with ethyl ether and then dissolved in 50 ml. of tetrahydrofuran. Triethylamine hydrochloride was insoluble in the tetrahydrofuran and was separated. The tetrahydrofuran solvent was then removed from the product under reduced pressure and the solid recrystallized from ethyl alcohol to give white N,N'-bis(perfluorobutyryl)perfluoroglutarhydrazidine, melting at 175°. The infrared spectra of this product showed identical absorption bands for the functional groups to those obtained from N-perfluorobutyrimidoyl-N'-perfluorobutyrylhydrazine.

   b. Addition of perfluoroalkylhydrazides to perfluoro-
       alkylnitriles

Although conditions were found, for model compounds, under which perfluoroacylhydrazidines could be successfully acylated by perfluoroacyl chlorides without premature ring

closure and loss of water, this system was not considered
particularly promising for high polymer formation. It is
apparent that the same type of intermediate polymer structure
(A in Eq. 1) would result if the perfluoroalkylhydrazides
could be added to perfluoroalkylnitriles. The perfluoroalkyl-
hydrazides are slightly acidic and such a reaction would not
be expected to take place in nonpolar solvents. However, we
found that the addition would occur if dimethylformamide were
used as both solvent and a catalyst. When this type of reaction
was carried out using perfluorobutyronitrile and perfluoro-
glutarhydrazide in dimethylformamide, as shown in Eq. 2, the
yields were 98% in both the initial addition reaction and in
the ring closure step. Ring closure could be accomplished by
treating the intermediate A, Eq. 2, with phosphorous pentoxide
or with acetic acid or by merely heating the intermediate
above its melting point in an open test tube.

The structure shown at A in Eq. 2, however, is not
the only structural group that would be formed in a polymer
produced in the reaction of perfluoroglutaronitrile and perfluoro-
glutarhydrazide. Such a polymer would also contain sections
in which the fluorocarbon chains would have amino or imino
groups on both sides or have carbonyl or hydroxyl groups on
both sides as shown in Eq. 3. Here it will be noted that

Eq. 2
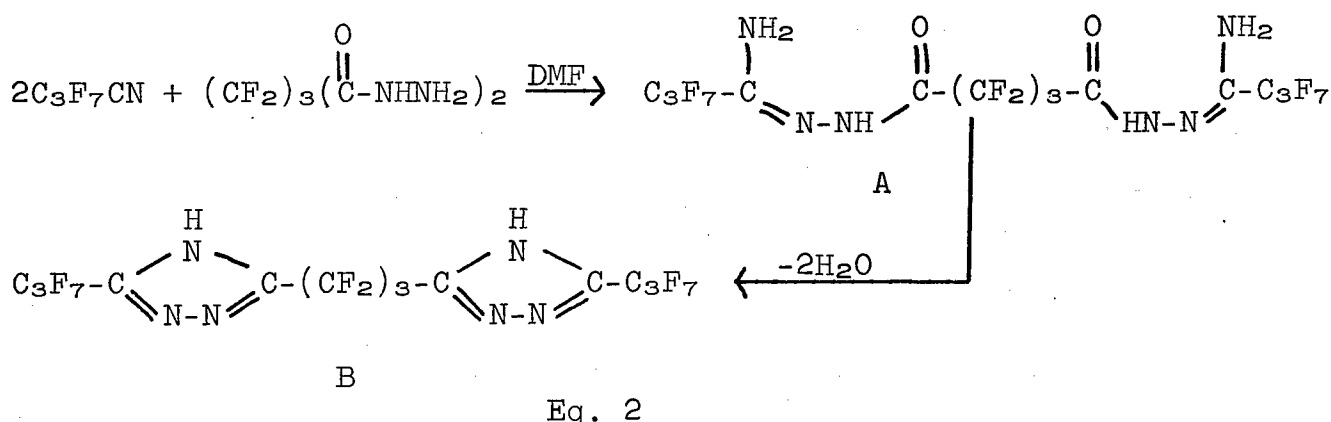
Section C has two amino groups at the end of the perfluoroalkylene
chain and Section D has two carbonyl (or hydroxyl) groups at the
end of the next perfluoroalkylene chain.

Eq. 3

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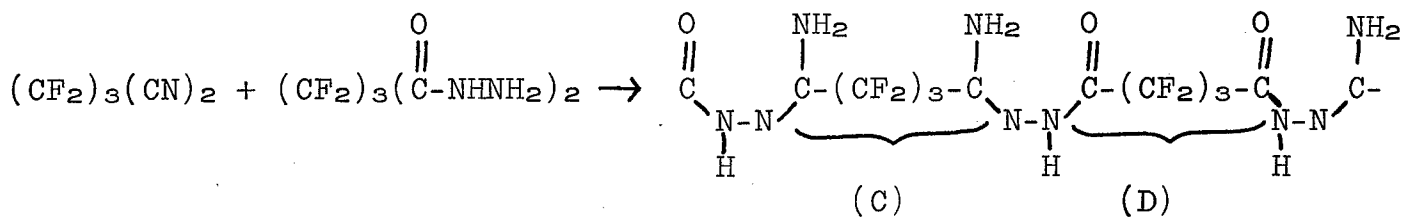
In order to determine the effects of the structural groups shown at C in Eq. 3 on the subsequent ring closure, a model compound having this structure was synthesized from perfluoroglutaronitrile and perfluoroglutarhydrazide as shown in Eq. 4. The yields in this reaction ranged from 30-40%.

$$2C_3F_7\overset{O}{\overset{\|}{C}}-NHNH_2 + (CF_2)_3(CN)_2 \rightarrow C_3F_7-\overset{O}{\overset{\|}{C}}\underset{N-N}{\diagdown}\overset{NH_2}{\overset{|}{C}}-(CF_2)_3-\overset{NH_2}{\overset{|}{C}}\underset{N-N}{\diagdown}\overset{O}{\overset{\|}{C}}-C_3F_7$$

(E)
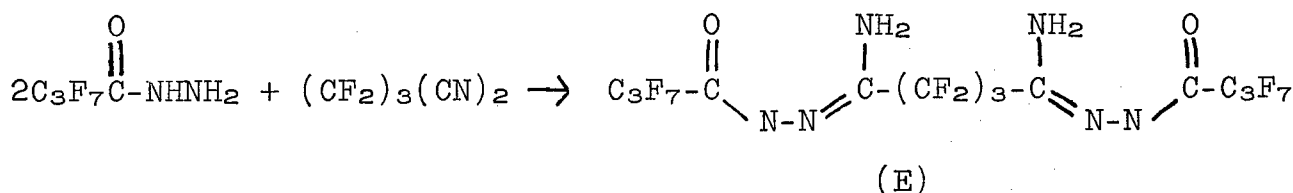
Eq. 4

When the product E was heated above its melting point under the same conditions used for the intermediate structure A in Eq. 2, it decomposed and did not produce the <u>bis</u>-triazole structure. Treatment of E with acetic acid gave a white solid which melted between 207-211°. The infrared spectrum of this product showed a strong broad band at $3.1-3.5\mu$, a sharp band at 5.76μ, a somewhat weaker band at 6.09μ, a strong band at 6.23μ, and also the strong band at 6.86, 7.10, 7.40 and 7.55μ, which are found in the spectra of the <u>bis</u>-triazole. Two of the possible structures resulting from the heating of the intermediate structure E with acetic acid are shown as II and III. Other structures are possible, of course, if the intermediate E

$$C_3F_7C\underset{N-N}{\overset{\diagup NH \diagdown}{\diagdown\diagup}}C(CF_2)_3\overset{NH_2}{\overset{|}{C}}\underset{N-NH}{\diagdown}\overset{O}{\overset{\|}{C}}-C_3F_7 \qquad \text{II}$$

$$C_3F_7\overset{O}{\overset{\|}{C}}\underset{NH-N}{\diagdown}\overset{C}{\overset{|}{\underset{CF_2}{}}}\overset{\diagup NH \diagdown}{}\overset{C}{\overset{|}{\underset{CF_2}{}}}\underset{N-NH}{\diagdown}\overset{O}{\overset{\|}{C}}-C_2F_7 \qquad \text{III}$$
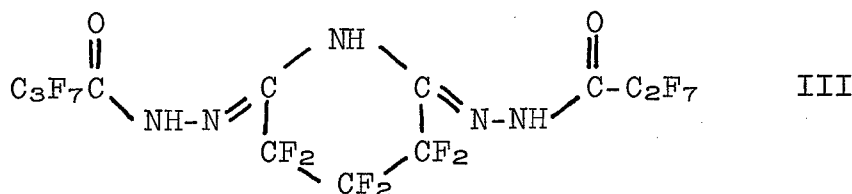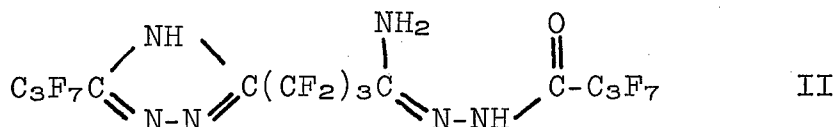
lost two moles of water to form the <u>bis</u>-triazole or evolved various combinations of ammonia and water to form partially cyclized products with oxadiazole or triazole rings or underwent even further reaction with hydrolysis of the imino groups by the evolved water.

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Subsequent treatment appeared to show that the product obtained from heating the intermediate E with acetic acid was indeed a mixture of products. When this mixture was dissolved in dilute sodium hydroxide and reprecipitated by acidifying the basic solution the infrared spectra of the treated material showed a large decrease in intensity of the bands not identified with the bis-triazole structure. However, pure bis-triazole was not obtained from repeated treatment of the solid with dilute base followed by acidification. When the original product E was heated in boiling methanol and water a white solid was obtained which melted between 190-210° and had an infrared absorption spectrum almost identical to the spectra of the solids obtained from perfluorobutyrhydraizine hydrochloride and perfluorobutyryl chloride.

The structure shown as III, which would result from cyclization by the loss of ammonia from the amino groups at either end of the perfluoroalkylene chain has not been isolated but appears at this time to be a distinct possibility. If cyclization of this type occurs, it would of course eliminate the possibility of forming triazole rings throughout the polymer chain.

Since it is obvious from the work with perfluoro-glutaronitrile and perfluorobutyrhydrazide that the presence of amino groups at the ends of a perfluoropropylene chain may cause unwanted cyclization reactions to take place, the use of a longer chain dinitrile was indicated for polymerization reactions.

The first reactions using a longer chain perfluoro-alkyldinitrile were model reactions between perfluorobutyrhydrazide and perfluorosebaconitrile. Addition took place in a dilute dimethylformamide solution at 65° to yield 90% of N,N'-bis-(perfluorobutyryl)perfluorosebachydrazidine. It is important that in this initial reaction there be no ring closure to the triazole structure with the evolution of water for, although the intermediate compound probably would not be hydrolized by the water, hydrolysis of the remaining dinitrile in the polymerization reaction would most certainly reduce the degree of polymerization.

Yields ranging from 90-96% of 1,3-bis(perfluoro-propyl-1,2,4-triazolyl)perfluorooctane were obtained by heating the N,N'-bis(perfluorobutyryl)perfluorosebachydrazidine in refluxing acetic acid or by heating this intermediate alone at 190° for 8 hr. in an open test tube. When this intermediate compound was heated in refluxing acetic acid the product containing triazole rings did not precipitate from the solution even after the solution was cooled in an ice bath. This solubility property of the 1,8-bis(perfluoropropyl -1,2,4-triazolyl)-perfluorooctane was quite different from that of the 1,3-bis(perfluoropropyl-1,2,4-triazolyl)perfluoropropane The latter compound was almost completely insoluble in refluxing acetic acid.

The first polymeric acylhydrazidines were obtained from the reaction of perfluorosebaconitrile and perfluoroglutar-hydrazide in dimethylformamide. The actual structure of the products obtained from these reactions was dependent upon the temperature and reaction time. At 110°, 70°, and also at 50° a polymeric product was obtained which had acyclic acylhydrazidine links as well as triazole rings in the structure. When the reaction was carried out at 35° and for shorter lengths of time the polymeric material apparently did not undergo dehydration and no triazole rings were formed. The infrared spectra the polymer obtained at the lowest temperature was almost identical with the infrared spectra of the model compound discussed previously, the only difference being the appearance of a band at 7.38μ in the model compound, which had been attributed to the CF_3 group, and which would, of course, not be present in the polymeric material.

The intermediate acyclic polymer prepared from perfluorosebaconitrile and perfluoroglutarhydrazide was cyclized by dehydration by heating it either in refluxing glacial acetic acid or in refluxing perfluorobutyric acid and could also be cyclized by heating alone at 200° under reduced pressure. The polymeric acyclic intermediate was insoluble in perfluoro-butyric acid and the polymer containing triazole rings was insoluble in both acetic and perfluorobutyric acid. The infrared spectra of these products indicated that dehydration and cycliza-tion was not complete. The spectra contained absorption bands at 5.78 and 6.02μ in addition to the bands at 6.86, 7.10, 7.40 and 7.55μ. These latter bands are characteristic of the triazole model compound. The bands at 5.78 and 6.02μ could be characteristic either of end-groups or acyclic links in the polymer chain.

It seems quite possible that, in the acid solutions, partial ring closure along the polymer chain could result in increasing insolubility of the polymer, thus precipitating it from the solution and hindering, if not completely inhibiting, further ring closure. If this is occurring, it would be desirable, of course, to keep the polymer in solution until dehydration was complete. The model compound containing two triazole rings from perfluorosebaconitrile and perfluorobutyrhydrazide was soluble in acetic acid. From this result it appeared that the longer chain material having a smaller percentage of weight due to triazole rings is more soluble in acetic acid and it also appeared that replacement of the perfluoroglutarhydrazide with a longer chain dehydrazide might produce a triazole polymer that was soluble in acetic acid.

For this purpose perfluorosebachydrazide was prepared by adding a methanol solution of the ester to a small excess of hydrazine dissolved in methanol. The reaction proceeded readily at room temperature. Although rather crude ester was used in this reaction a very pure product, melting at 201.5-202.0°,

was obtained. The infrared spectra of this hydrazide showed all the characteristic peaks of the previously prepared mono and dehydrazides. Attempts at recrystallization (from a mixture of methanol-isopropyl ether) and at sublimation under reduced pressure lowered the purity of the product. The best preparative procedure found to date involves washing the initial product several times with ice-cold methanol and drying under reduced pressure.

In the polymerization reactions between perfluoro-sebaconitrile and perfluoroglutarhydrazide two principal factors apparently influenced the degree of polymerization. The first of these was the insolubility of the intermediate polymer in the various solvents used and the second was the presence of water resulting from ring closure of the intermediate during the initial polymerization reaction. The initial reactions of perfluorosebaconitrile with perfluorosebachydrazide indicated that these two factors must be considered carefully in this system.

The reaction of perfluorosebaconitrile with perfluoro-sebachydrazide in dimethylformamide was carried out at 45° and at this temperature an acyclic polymer was obtained. However, precipitation of the polymer began after three hours reaction time and this insolubility may have contributed to the relatively low molecular weight. Of the intermediate polymer obtained, 40% was insoluble in DMF at the concentrations used and 60% was soluble. Both the soluble and insoluble polymers were dehydrated and cyclized in acetic acid at its reflux temperature to produce polytriazoles of approximately the same characteristics, melting range 260-275°, molecular weight approximately 2500.

The polymerization of perfluorosebaconitrile with perfluorosebachydrazide was also carried out in dimethylsulfoxide. This reaction mixture was heated at 80° for six days and during this period a white solid precipitated. The reaction temperature was raised to 100° and held at this temperature for four days but the product did not dissolve. The reaction mixture was cooled to room temperature and solid product separated by filtration. Dilution of the dimethylsulfoxide with benzene produced no additional solid polymer. The infrared spectra of this product showed that some cyclization had occurred and that triazole rings were present. Cyclization was completed by heating in acetic acid to give a product with a melting range of 265-275°.

c. Treatment of end-groups of the poly(perfluoroalkylene-1,2,4,4H-triazoles

To obtain a true picture of the thermal stability and chemical characteristics of the poly(perfluoroalkylene-1,2,4,4H-triazoles) it will be desirable to convert the end-

groups, whether C≡N or C(=O)NH₂, to a more unreactive species. Our approach to this problem has been to hydrolyze the end-group to a carboxyl group by the use of aqueous sodium hydroxide solution, and to decarboxylate the terminal COOH group to convert the chain ends to CF_2H.

A sample of the polymer obtained from perfluorosebaconitrile and perfluoroglutarhydrazide was refluxed in sodium hydroxide solution for three days. The basic solution was then acidified with hydrochloric acid and the resulting precipitate removed by filtration and dried. Hydrolysis of the end-groups had taken place and the infrared spectra of the dried polymer showed a band at 5.62μ for the acid carbonyl (a shift from the 5.78μ band present in the spectra of the polymer before treatment with the aqueous base) and a broad band at 2.9μ for the acid hydroxyl groups.

For the decarboxylation of the hydrolyzed end-groups, the polymer was placed in ethylene glycol and refluxed for two days. Recovery of the polymer, after strong acidification of the solution, gave a product whose infrared spectra show no evidence of acid end-groups and was quite characteristic of the model perfluoroalkyl-substituted triazoles. This procedure had evidently converted the carboxyl end-groups to CF_2H groups in accordance with the normal decarboxylation reaction of perfluoroalkyl-carboxcylic acids.

A sample of the polytriazole prepared from perfluorosebaconitrile and perfluorosebachydrazide in dimethylformamide was refluxed for 2 1/2 days in 10% sodium hydroxide. The polymer was insoluble and the aqueous solution and was separated by filtration, then dried at 110° for two hours under reduced pressure. The infrared spectra of this product, the sodium salt of the polytriazole, showed no absorption in the OH stretching region. The sodium salt of the polymer was placed in ethylene glycol and refluxed for two days, then heated at 230° for two days under reduced pressure. This procedure produced a very tacky product which was then heated on a water bath with aqueous HCl for six hours. The recovered polymer from the aqueous HCl was heated at 260° for two hours under reduced pressure and became brittle. This brittle polymer did not dissolve but did swell in tetrahydrofuran on standing.

A sample of the polytriazole prepared from perfluorosebaconitrile and perfluorosebachydrazide in dimethylsulfoxide was refluxed for two days in 10% sodium hydroxide solution. The insoluble sodium salt of the polymer was then recovered and dried at 110° for two hours under reduced pressure. Decarboxylation of the acid end-groups was accomplished by refluxing the sodium salt in ethylene glycol for 24 hours. The ethylene glycol solution was added to 100 ml. of hydrochloric acid to precipitate the polymer, which was then dried at 120° for two hours under

reduced pressure. The melting point of this polytriazole was
265-275° and the molecular weight 4400. The infrared spectra
of this material showed the characteristic absorption bands of
the model triazole compounds.

> d. <u>Reaction of triazole model compounds with sodium
> hydroxide</u>

In the reactions described above for the hydrolysis
of the end-groups of the polytriazole with sodium hydroxide it
is evident that the strongly acidic proton of the triazole ring
will also be removed and that the sodium salt of the triazole
rings will be present. To determine the affects of this salt
formation on the ring structure, a sodium salt of a model
compound without carboxyl groups was prepared and investigated.

3-Perfluoropropyl-5-perfluoroethyl-1,2,4-triazole
was neutralized with sodium hydroxide solution and the solution
evaporated to dryness under reduced pressure. This material
was very hygroscopic but an infrared absorption spectrum was
obtained by preparing a mull of the dried material in Kel-F
oil under a nitrogen atmosphere. This spectra showed absorption
maxima at 6.64 and 6.85μ but no absorption between 2.0 and
6.5μ. The peak at 6.85 is in the region of the peak found
in the free triazole and the peak at 6.64μ is in the region of
a very weak band found in the free triazole. When this sodium
salt was heated at 250° under reduced pressure, a yellow
tacky material sublimed to the upper wall of the tube. The
infrared spectra of the sublimate and of the residue from this
procedure was quite different from the original sodium salt
and a reaction obviously had taken place. The nature of this
reaction has not yet been determined.

To demonstrate that the triazole could be recovered
from the sodium salt if the salt were not heated to the temperature
described in the preceding paragraph, the sodium salt of 1,3-<u>bis</u>-
(perfluoropropyl-1,2,4-triazolyl)perfluorooctane was prepared
by refluxing this material for two hours in 10% sodium hydroxide
solution. The solution was evaporated to dryness under reduced
pressure to leave a white residue. The original <u>bis</u>-triazole
was obtained by warming this residue in aqueous <u>hydrochloric</u> acid.

> 3. <u>Heating perfluoroglutarhydrazidine with excess hydrogen
> chloride</u>

The previous technical report[1] described a reaction
wherein perfluorobutyrhydrazidine hydrochloride was heated to
yield 50% 3,6-<u>bis</u>(perfluoropropyl)-1,2-dihydrotetrazine. During
the present period this heating procedure was extended to
perfluoroglutarhydrazidine in the presence of hydrogen chloride
in an attempt to obtain a polymer having dihydrotetrazine groups
in the chain. The perfluoroglutarhydrazidine was heated in a
sealed tube with an excess of hydrogen chloride and with tetra-
hydrofuran as a solvent. The product obtained was an amber solid
whose infrared spectra indicated that it contained the imidoyl-

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hydrazidine structure. It seems possible that under the conditions used for this experiment the perfluoroglutarhydrazidine formed the cyclic monomer described above, 1,2-diaza-3-imino-7-amino-4,4,5,5,6,6-hexafluorocycloheptene-7, which subsequently polymerized to give the imidoyl-hydrazidine linear polymer structure.

B. Poly(perfluoroalkylene-1,3,4-oxadiazoles)

1. From perfluoroglutarylchloride and 1,3-bis(5-tetrazolyl)-perfluoropropane

A previous report [4] mentioned briefly the reaction of 1,3-bis(5-tetrazolyl)perfluoropropane with perfluoroglutaryl-chloride to form poly(perfluoroalkylene-1,3,4-oxadiazole) directly as shown in Eq. 5. During the present period this type of polymerization reaction was carried out in anhydrous xylene at atmospheric pressure and at an initial temperature of 120°. As the molecular weight of the polymer produced increased, it precipitated from the solution and adhered to the walls of the

$$(CF_2)_3 \left(C \begin{array}{c} N=N \\ | \\ N-NH \end{array} \right)_2 + (CF_2)_3(COCl)_2 \rightarrow \left[(CF_2)_3 - C \begin{array}{c} O \\ N-N \end{array} C \right]_n$$
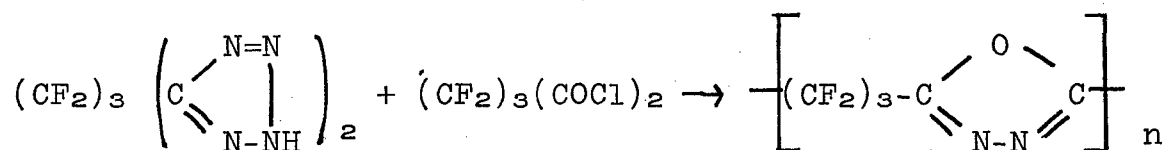
Eq. 5

reaction flask. After addition of the perfluoroglutaryl-chloride was complete, the reaction mixture was heated to the reflux temperature of xylene (about 140°) and maintained at this temperature for 20 hours.

The xylene-insoluble polymer was dried under reduced pressure for 8 hours at room temperature to give a product which was insoluble in diethylether and acetone but soluble in hot acetylnitrile and hot tetrahydrofuran. A small sample decomposed, as expected, when heated in 5% sodium hydroxide solution; a similar heating procedure in 50% nitric acid did not decompose or dissolve the polymer.

The crude, brown xylene-insoluble polymer began to melt at 130° but did not flow until the temperature of 180° had been reached. A portion of this crude solid was dissolved in· hot acetylnitrile and a film made on a sodium chloride plate. The infrared spectra showed essentially no carbonyl absorption but did show a characteristic oxadiazole band at 6.3μ. A molecular weight determination of the crude xylene-insoluble product gave a value of 2600 (VPO).

A 0.25 g. portion of the crude oxadiazole polymer was placed in a sublimation apparatus and heated under vacuum at 160° for 1 hr. in an attempt to remove low molecular weight material. The light tan solid turned dark brown as the heating progressed. The residue from this treatment was dissolved in hot acetonitrile and the solution allowed to cool. A light tan solid product separated from this solution (approximately 88% of the original material); the molecular weight of this solid determined in tetrahydrofuran was 6800 and its m.p. was 165-230.

A similar polymerization using the silver salt of 1,3-bis(5-tetrazolyl)perfluoropropane and perfluoroglutaryl chloride was attempted but only products of very low molecular weight were obtained. The principal difficulty involved in using the silver salt of the bis-tetrazole appears to lie in our inability to completely dry this monomer. Drying under reduced pressure at 60° gave a product whose infrared spectra did not seem to indicate the presence of moisture but apparently there did remain traces of water in the product. This water, of course, would hydrolyze the perfluoroglutaryl chloride and terminate chain formation.

Since the poly(perfluoroalkylene-1,3,4-oxadiazole) is insoluble in xylene a search has been made for other solvents in which the polymerization could be carried out. A suitable solvent would boil at sufficiently high temperatures to allow heating of the reactants to the reaction temperature of the bis-tetrazole, dissolve the resulting polymer, and not be effected by the evolved hydrogen chloride. Diethyleneglycol dimethylether was found to be a solvent for the polymer produced in xylene and attempts have been made to use this material as a solvent for the polymerization reaction. The diglyme solvent was distilled from barium oxide under reduced pressure and from lithium aluminum hydride under reduced pressure and this process should have eliminated any traces of moisture or OH groups. However, in the polymerization reaction the solvent was heated at 135° in the presence of hydrogen chloride and this apparently caused a decomposition to take place. The procedures of polymerization using diglyme as a solvent are described in the Experimental Section in detail; from this work only oils have been obtained.

A further attempt was made to carry out the reaction between perfluoroglutaryl chloride and 1,3-bis(5-tetrazolyl) perfluoropropane using acetic acid as a solvent. Both monomers and the polymer previously produced in xylene are soluble in this solvent. However, runs made in acetic acid apparently involved side reactions which severely inhibited polymerization. Several of these may be considered to have been competing with acylation of the perfluoroalkyltetrazole. For example, perfluoroglutaryl chloride could have reacted with acetic acid to form acetic anhydride, which could then acylate the tetrazole and terminate the polymerization process. In all probability several

different types of reactions occurred in this attempted polymerization. Upon examination of the infrared spectra of the reaction products, which were oils, no absorption maxima characteristic of the oxadiazole ring could be found. Heating the isolated oils under reduced pressure for prolonged periods of time at elevated temperatures still produced no oxadiazole rings.

Even in the event that acylation of the tetrazole was accomplished only by perfluoroglutaryl chloride, there is still a possibility that the reactive intermediate which results from the loss of nitrogen would undergo reaction with the easily released proton of the acetic acid rather than ring closure to the oxadiazole structure. No further polymerization attempts will be made using this type of solvent.

The Experimental Section of this report describes a modified preparation of 1,3-bis(5-tetrazolyl)perfluoropropane which is a considerable improvement over the previously used method.

The use of bitetrazole (structure A in Eq. 6) for the production of a model compound incorporating the bioxadiazole structure was mentioned previously.[4] Reaction of this material with perfluoroglutaryl chloride should produce a polymer with the bioxadiazole unit in it as shown at B in Eq. 6.

$$
\begin{array}{c}
\text{(structure A)} + (CF_2)_2(COCl)_2 \rightarrow \text{(structure B)}_n
\end{array}
$$

A.   B.
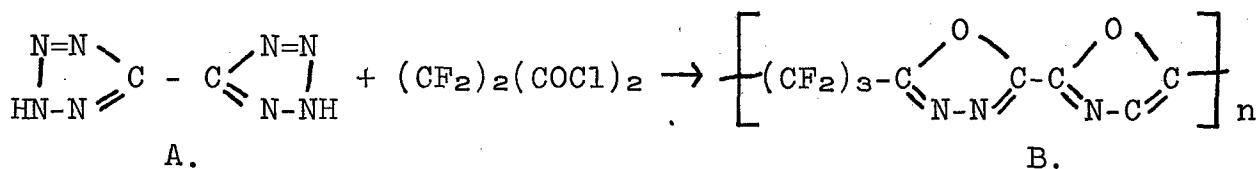
Eq. 6

In order to prepare high purity bitetrazole, considerable effort has been devoted during the present period to modification of the method of synthesis for this material described in the literature.[3] The procedure adopted produces the disodium salt of bitetrazole; generation of free bitetrazole was not acheived by acidifying a solution of the disodium salt with nitric acid. The material obtained from this procedure was apparently the monosodium salt which detonated at 310° rather than melting at 256° as is reported for bitetrazole. The free bitetrazole was obtained by converting the sodium salt to the mecuric salt with mecuric nitrate and precipitating the mercury by addition of hydrogen sulfide.

Polymerizations using bitetrazole have not yet been carried out.

2. From perfluoroglutarylchloride and perfluoroglutarhydrazide

Another approach to the problem of synthesis of polyperfluoroalkylene-1,3,4-oxadiazoles involving the acylation of perfluoroglutarhydrazide with perfluoroglutarylchloride to produce a poly(perfluoroalkylene-N,N'-diacylhydrazine), as shown in Eq. 7 has been continued during the present period. A

$$(CF_2)_3(COCl)_2 + (CF_2)_3(CONHNH_2)_2 \rightarrow \left[(CF_2)_3\!-\!\overset{\overset{O}{\|}}{C}\!-\!NHNH\!-\!\overset{\overset{O}{\|}}{C}\right]$$

$$\downarrow -H_2O$$

$$\left[(CF_2)_3\!-\!C\!\underset{N-N}{\overset{O}{<}}\!C\right]_n \longleftarrow$$

Eq. 7

previous report [4] discussed the polymerization of perfluoroglutarhydrazide with perfluoroglutarylchloride in a number of basic solvents such as hexamethylphosphoramide, cyclohexanone, and dimethylformamide and also in an acidic solvent, in particular, acetic acid. Due to the inductive effect of the perfluoroalkylene group, perfluoroglutarhydrazide is slightly acidic and of course the resulting diacylhydrazine group in polymer would also be acidic. Reaction with the basic solvents might therefore occur and, in fact, in the products previously obtained there appeared to be considerable amounts of the solvent incorporated. In the previous work the best solvent found for this reaction was acetic acid.

During the present period a determined attempt was made to obtain anhydrous, pure acetic acid. Reagent grade glacial acetic acid was first distilled and the portion boiling at 118° collected. This portion was then refluxed with potassium permanganate, redistilled and the fraction boiling at 118° again collected. This fraction was then distilled from an excess of triacetylborate, collected, and stored under dry nitrogen.

Perfluoroglutarhydrazide for the polymerization reaction was prepared by the reaction of diethylperfluoroglutarate with hydrazine. The slightly yellow, crude product was filtered, dried under reduced pressure for three days, then digested with isopropyl ether to remove excess alcohol and the yellow color. The melting point of the dihydrazide at this stage was 164-166°. This product was then redissolved in boiling methanol, filtered, and isopropyl ether added to the methanol solution. Crystallization of perfluoroglutarhydrazide occurred from this mixture of solvents and gave a product which melted, after drying, at 168-169°.

In carrying out the polymerization reaction in acetic acid, a white precipitate appeared as the acylchloride was added to the solution of the hydrazide at 25°. Although this material was not isolated it is possible that it is a hydrochloride formed from the hydrazide end-groups after the initial reaction of one acylchloride group with one hydrazide group. If this is the type of reaction that is occurring then all of the acid chloride would be trapped into an intermediate of the type shown as IV. At higher temperatures a further

$$\underset{\text{Cl}\overset{\displaystyle O}{\overset{\|}{C}}-(CF_2)_3\overset{\displaystyle O}{\overset{\|}{C}}\diagdown_{NHNH}\diagup\overset{\displaystyle O}{\overset{\|}{C}}(CF_2)_3\overset{\displaystyle O}{\overset{\|}{C}}\diagdown_{NHN\overset{+}{H}_3\cdot Cl}}{}\qquad IV$$
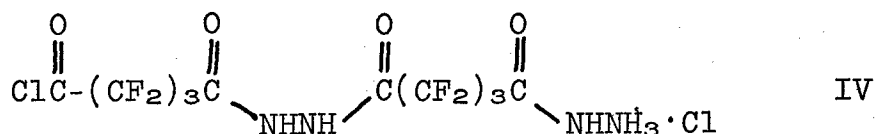
reaction would occur and the hydrazide hydrochloride group should be acylated by the acylchloride groups.

The poly(perfluoroalkylene-diacylhydrazine) formed in acetic acid has proven to be very difficult to separate from the solvent. The best procedure developed involved the removal of most of the solvent under reduced pressure at a temperature of about 80°. The very viscous oil remaining was transferred to a tube and kept under reduced pressure 140° for 24 hours; however, traces of acetic acid still remained. The polymers formed in this solvent were water soluble and therefore traces of the acetic acid could not be removed with sodium bicarbonate solution.

The polymerization of perfluoroglutarhydrazide with perfluoroglutaryl chloride has also been investigated using anhydrous dioxane as a solvent. In this solvent a reaction similar to that described above apparently took place to form the hydrochloride salt as shown in Fig. 10. Elimination of hydrogen chloride began as the temperature of the reaction mixture was raised.

Molecular weights (VPO) of the crude, pale brown, solid polymers obtained in the initial runs were in the 1700-1800 range. When this product was held at 200-250° under reduced pressure some low molecular weight material was lost and this treatment gave a light brown polymer with a molecular weight of about 3000.

A later polymerization of perfluoroglutarhydrazide and perfluoroglutarylchloride was carried out in dioxane using more elaborate precautions to exclude moisture from the solvent and reactants. In this preparation the acid chloride was added dropwise to the hydrazide slurry and stirred overnight at room

temperature. Heating was then begun and hydrogen chloride evolution was observed at approximately 70° The temperature rose to 101° and the reaction mixture was held at this temperature until hydrogen chloride evolution had ceased (20 days). The dioxane was then removed under reduced pressure leaving a very viscous amber mass which was heated for four days at 160° to produce a light brown powder, soluble in acetone, tetrahydrofuran, methanol, and dimethylsulfoxide.

A small sample of this polymer was fractionated by dissolving it in methanol and precipitating the polymer by the addition of water. The first fraction had a molecular weight of about 3700 (m.p. 290°). This represents a degree of polymerization of approximately 16. Two subsequent fractions melted at 285° The lowest molecular weight fraction also melted at 285° and was found to have a molecular weight of 3400.

The reaction of perfluoroglutarylchloride and perfluoroglutarhydrazide in dioxane appears to be a clean one and the principal difficulty in obtaining higher molecular weight is undoubtedly the presence of traces of water in the system. At the present time dioxane appears to be the most convenient solvent and has the added advantage that the reaction can be monitored by observing the disappearance of the acyl-chloride band at 5.55μ and the appearance of the diacyl-hydrazine carbonyl doublet at 5.60 μ and 5.78μ on samples removed from the reaction flask.

The polymers prepared in this system will be used to study possible methods of dehydration to form the 1,3,4-oxadiazole ring.

III. EXPERIMENTAL

A. Poly(perfluoroalkylene-1,2,4,4<u>H</u>-triazoles)

1. Heating perfluoroglutarhydrazidine in the presence of hydrogen chloride

Perfluoroglutarhydrazidine, 3.0 g. (0.0131 moles), was placed in a heavy-wall glass tube of approximately 120 ml. capacity. After the air was removed from the tube by pumping, 0.044 moles of dry hydrogen chloride and 25 ml. of tetrahydrofuran were passed through a phosphorus pentoxide tube and condensed into the reaction tube. The reaction tube was then sealed and heated at 100° for nine days, cooled to room temperature and opened. The tetrahydrofuran solution was filtered and the precipitate washed with a small amount of tetrahydrofuran. The remaining tan solid was washed with water which showed a positive test for chloride ion. The tetrahydrofuran filtrate was added to cold water and 2.0 g. of amber solid obtained. The infrared spectra of both the tetrahydrofuran soluble and insoluble material showed that they contained the imidoyl-hydrazidine structure.

2. Reactions of the cyclic monomer(I)

a. With polyphosphoric acid

The cyclic monomer (I),[1] 2.0 g. (0.007 moles) and 25 ml. of polyphosphoric acid were placed in 100 ml. flask fitted with a water cooled condenser. The flask was heated at 175° for 12 hr. and the resulting dark slurry added to water. The dark solid which precipitated from the aqueous solution was washed twice with warm water and dried. The infrared spectra did not show the typical absorption due to the perfluoroalkyl-substituted triazole ring.

b. With acetic acid in <u>bis</u>(2-ethoxyethyl)ether

The cyclic monomer (I), 4.0 g. (0.015 moles), and 20 ml. of glacial acetic acid in 15 ml. of <u>bis</u>(2-ethoxyethyl) ether were placed in a heavy-wall glass tube. After the air was removed from the tube by pumping, the tube was sealed and heated at 110° for 40 hr. and at 150° for 86 hr. The tube was then opened and the solution added to ice water. A dark solid, 3.0g., was obtained; this product remained dark after being precipitated twice from tetrahydrofuran by dilution with water. The infrared spectra of this material did not indicate the presence of the triazole ring.

c. With excess hydrogen chloride

The cyclic monomer (I), 3.0 g. (0.013 moles) was placed in a heavy-wall glass tube and the air removed by pumping. Dry hydrogen chloride, 0.14 moles, was condensed in the tube which was then sealed and heated in the following manner: 72 hr. at 125°, 96 hr. at 185°, and 48 hr. at 215°. The tube was then cooled and opened and the tan solid recovered from the reaction was further heated under reduced pressure at 225° for 8 hr. to remove the ammonium chloride formed. The tan solid polymer was then placed in tetrahydrofuran and 0.35 g. was found to be insoluble. The tetrahydrofuran solution of the soluble polymer was filtered and 2.25 g. of amber solid was obtained by adding the filtrate to cold water. The solid polymer which precipitated from water was heated under reduced pressure at 375° for 8 hr. during which the material darkened and became insoluble in tetrahydrofuran. This material was placed in 10% sodium hydroxide solution and after two weeks about 30% had dissolved. This base-soluble portion was recovered by acidification and was found to be insoluble in tetrahydrofuran; its infrared spectra indicated that the material did contain the triazole structure.

d. In diglyme with acetic acid

The cyclic monomer from the reaction of perfluoro-glutaronitrile and hydrazine, 4.3 g., .018 moles, 17 ml. of glacial acetic acid, and 25 ml. of diglyme were placed in a heavy-wall, glass tube. After the tube was pumped free of air, it was sealed and heated at 115° for 48 hr. and then further heated at 135° for 90 hr. During this heating period the solution became very dark. The tube was cooled, opened, and its contents added to 50 ml. of ice water. After standing overnight, 0.75 g. of dark brown solid precipitated from the aqueous solution. The I.R. spectra of this solid showed no evidence of the triazole structure.

e. In methyl carbitol with acetic acid

The cyclic monomer, 3.0 g., 0.0128 moles, 30 ml. of glacial acetic acid, and 20 ml. of methyl carbitol were placed in a heavy-wall, glass tube. After the tube was pumped free of air, it was sealed and heated at 90° for 12 hr. and then further heated at 140° for 5 days. During this heating period the solution became very dark. The tube was cooled, opened, and its contents added to 50 ml. of ice water. After standing overnight, 0.5 g. of dark brown solid precipitated from the aqueous solution. The I.R. spectra of this solid showed no evidence of the triazole structure.

3. Acylation of perfluoroalkyl hydrazidines

a. Reaction of perfluorobutyrhydrazidine hydrochloride with perfluorobutyryl chloride

Perfluorobutyrhydrazidine hydrochloride, 2.0 g. (0.0082 moles) and 30 ml. of diethyl ether were placed in a heavy-wall glass tube. The air was removed from the tube and 0.0082 moles of perfluorobutyrylchloride were condensed in the tube which was then sealed and gradually heated to 70°. At this temperature, which was maintained for 15 hr., a solid precipitated from the solution.

The reaction tube was cooled and opened and the ether solution filtered. The filtrate was evaporated under reduced pressure to yield 3.5 g. of white solid whose infrared spectra indicated that it was a mixture of 3,5-bis(perfluoropropyl)-1,2,4-triazole and 1,2-bis(perfluorobutyryl)hydrazine. Attempts to separate the mixture by recrystallization, sublimation, or acidification were unsuccessful.

b. Reaction of perfluoroglutarhydrazidine with perfluorobutyryl chloride

1. By heating at 50°

Perfluoroglutarhydrazidine, 4.0 g. (0.015 moles) was placed in a heavy-wall glass tube and the air removed by pumping. Perfluorobutyryl chloride, 18 ml. , was condensed into the tube which was then sealed and heated at 50° for 18 hr. After the tube was cooled and opened, the excess butyryl chloride was removed under reduced pressure. The spectra of the remaining dark, tacky material showed that it contained the imidoyl hydrazidine structure.

2. In the presence of triethylamine

Perfluoroglutarhydrazidine, 3.8 g. (0.0144 moles), triethylamine, 4.0 ml., and carbon tetrachloride, 75 ml., were placed in a 250 ml. two-neck flask. The flask was fitted with a dry ice condenser and dropping funnel containing 9.2 g. (0.04 moles) of perfluorobutyryl chloride. The hydrazidine slurry was cooled in an ice bath and stirred while the perfluorobutyryl chloride was added dropwise. After the addition was complete, the contents of the flask was stirred for 1 hr. The resulting slurry was filtered and the solid material washed with ethyl ether, then placed in 50 ml. of tetrahydrofuran. A white solid which was insoluble in tetrahydrofuran was removed by filtration and was identified as triethylamine hydrochloride. The tetrahydrofuran solution was evaporated under reduced pressure and 2.5 g. of white solid product obtained. After recrystallization from ethanol this product, N,N'-bis(perfluorobutyryl)perfluoroglutarhydrazidine, melted at 175° and gave an infrared spectrum which showed the characteristic bands of the previously determined spectra of N-perfluorobutyrimidoyl-N'-perfluorobutyryl hydrazine.

4. <u>Addition of perfluoroacyl hydrazides to perfluoroalkyl</u>
   <u>nitriles (model structures)</u>

    a. <u>Reaction of perfluoroglutarhydrazide and perfluoro-</u>
   <u>butyronitrile</u>

        Perfluoroglutarhydrazide, 3.99 g., 0.015 moles, and
20 ml. of DMF were placed in a heavy-wall, glass tube. After the
tube was pumped free of air, perfluorobutyronitrile, 5.85 g.,
0.030 moles, was condensed into the tube which was then sealed
and heated at 80° for 5 hr. The tube was cooled, opened, and
the contents added to 50 ml. of ice water. The white precipitate
obtained from the aqueous solution was washed with acetonitrile
and 9.64 g., 98% yield, m.p. 199-201°, of N,N'-<u>bis</u>(perfluoro-
butyrimidoyl)perfluoroglutarhydrazide was obtained.

    b. <u>Reaction of perfluorobutyrhydrazide and perfluoro-</u>
   <u>glutaronitrile</u>

        Perfluorobutyrhydrazide, 7.52 g., .033 moles, were
placed in a heavy-wall, glass tube, after which perfluoroglutaro-
nitrile, 3.23 g., .016 moles, and 20 ml. of THF were passed
through a P_2O_5 column and then condensed into the tube. The
tube was pumped free of air, sealed, and heated at 50°for 1 1/2 hr.
During this heating period the solution became yellow and a white
solid precipitated from the solution. The tube was cooled, opened,
and its contents filtered. A white solid, 2.0 g., m.p. 194° (dec.),
was obtained. The THF solution was evaporated under reduced
pressure and 8.2 g. of yellow, tacky material was obtained.

    c. <u>Reaction of perfluorobutyrhydrazide with perfluoro-</u>
   <u>sebaconitrile</u>

        Perfluorosebaconitrile, 1.5 g., (0.0033 moles),
perfluorobutyrhydrazide, 1.51 g., (0.0066 moles) and 20 ml. of
dimethylformamide were placed in a heavy-wall glass tube which
was then pumped free of air, sealed, and heated at 65° for 24 hr.
The reaction tube was then cooled, opened and its contents added
to 100 ml. of cold water to precipitate 2.7 g. (90%) of
N,N'-<u>bis</u>(perfluorobutyryl)perfluorosebachydrazidine, m.p. 196-198°.

5. <u>Ring-closure of model hydrazide-nitrile reaction products</u>

    a. <u>Dehydration of N,N'-bis(perfluorobutyrimidoyl)perfluoro-</u>
   <u>glutarhydrazide</u>

       1. <u>By heating</u>

        N,N'-<u>bis</u>(Perfluorobutyrimidoyl)perfluoroglutarhydrazide,
1.0 g., 0.0015 moles, were placed in a test tube and heated at
200° for 8 hr. The white solid appeared to soften but did not melt.
The contents of the tube were then heated at 110° for 5 hr. under
reduced pressure to remove any water present. Obtained from the
tube was 0.91 g., 97% yield, of 1,3-<u>bis</u>(perfluoropropyl-1,2,4,4<u>H</u>-
triazolyl)perfluoropropane.

2. With P₂O₅

N,N'-<u>bis</u>(Perfluorobutyrimidoyl)perfluoroglutarhydrazide,
1.0 g., (0.0015 moles) and a large excess of P₂O₅ were placed in
a water cooled sublimation apparatus. The apparatus was heated at
60° for 15 hr. and then further heated at 150° for 8 hr. under
reduced pressure. During the heating period under reduced
pressure 0.75 g., 80% yield, of 1,3-<u>bis</u>(perfluoropropyl-1,2,4,4<u>H</u>-
triazolyl)perfluoropropane was collected on the cold finger.

3. With glacial acetic acid

N,N'-<u>bis</u>(Perfluorobutyrimidoyl)perfluoroglutarhydrazide,
1.0 g., 0.0015 moles, and 20 ml. of glacial acetic acid were placed
in a single-neck, round-bottom flask which was fitted with a water
cooled condenser. The flask was heated until the solution began
to reflux and then held at this temperature for 3 days. The acidic
solution was cooled and added to 50 ml. of ice water. The
resulting white precipitate was filtered and 0.92 g., 93% yield
of 1,3-<u>bis</u>(perfluoropropyl-1,2,4,4<u>H</u>-triazolyl)-perfluoropropane.

4. With hydrogen chloride

N,N'-<u>bis</u>(Perfluorobutyrimidoyl)perfluoroglutar-
hydrazide, 1.0 g. , 0.0015 moles, were placed in a heavy-wall,
glass tube. After the tube was pumped free of air, hydrogen
chloride, 0.015 moles were condensed into the tube. The tube
was sealed and heated at 95° for 15 hr. During this heating
period the white solid darkened and after the tube was cooled
to room temperature a very small amount of liquid condensed on
the inside walls of the tube in addition to the dark solid. The
contents of the tube were taken up in THF and a small amount of
white solid which gave a positive test for chloride ion was
obtained by filtering the THF solution. The THF soluble portion
of the product was recovered by evaporating the solvent under
reduced pressure but the I.R. spectra of the recovered dark brown
solid was too indistinct for any structure determination to be made.

b. Attempted dehydration of N,N'-<u>bis</u>(perfluorobutyryl)-perfluoroglutarhydrazidine

1. By heating

N,N'-<u>bis</u>(Perfluorobutyryl)perfluoroglutarhydrazidine,
0.5 g., .0008 moles, were placed in a test tube and heated at
200° for 15 min. During this heating period the solid melted
and decomposed.

2. With acetic acid

N,N'-<u>bis</u>(Perfluorobutyryl)perfluoroglutarhydrazidine,
2.0 g., 0.003 moles, and glacial acetic acid, 25 ml. were placed
in a single-neck, round-bottom flask. The flask was fitted with
a water cooled condenser and then heated until the acidic
solution began to reflux. The flask was heated at this temperature

for 2 1/2 days. The flask was cooled and its contents added to 100 ml. of ice water. Recovered from the aqueous solution by filtration was 1.0 g. of pale yellow solid which had a melting range of 208-212°.

      c.   Dehydration of N,N'-bis(perfluorobutyryl)perfluoro-sebachydrazidine

        1.   By heating

        N,N'-bis(Perfluorobutyryl)perfluorosebacohydrazidine, 0.5 g. (0.00055 moles) was placed in an open test tube and heated at 190° for 8 hr. During this heating period 0.45 g. (96%) of white 1,3-bis(perfluoropropyl-1,2,4-triazolyl)perfluorooctane sublimed and collected on the upper walls of the test tube. The m.p. of this compound is 212°.

        2.   With glacial acetic acid

        N,N'-bis(Perfluorobutyryl)perfluorosebachydrazidine, 1.0 g., (0.0011 moles) and 25 ml. of glacial acetic acid were placed in a round-bottom flask fitted with a water-cooled condenser. The solution was refluxed for three days; during this heating period no solids precipitated from the liquid. The acetic acid solution was then added to 100 ml. of cold water and 0.95 g., (90%) of white 1,3-bis(perfluoropropyl-1,2,4-triazolyl)perfluoro-octane was obtained.

     6.   Polymerization of perfluorosebaconitrile with perfluoro-glutarhydrazide

        a.   Perfluorosebaconitrile, 3.3758 g. (0.0075 moles), perfluoroglutarhydrazide, 2.0021 g. (0.0075 moles), and 30 ml. of dimethylformamide were placed in a heavy-wall, glass tube which was then pumped free of air, sealed, and heated at 70° for 9 days. The tube was cooled, opened, and 200 ml. of benzene added to its contents. The cream-colored tacky solid which precipitated from the solution became brittle when dried under reduced pressure. The infrared spectrum of this polymer indicated that its structure consisted of some triazole rings as well as some linear structure in which ring closure had not yet taken place. This material darkened when heated at 260-330° but did not melt.

        b.   Perfluorosebaconitrile, 3.386 g. (0.0076 moles), perfluoroglutarhydrazide, 2.0368 g. (0.0076 moles), five drops of triethylamine and 30 ml. of dimethylformamide were placed in a heavy-wall glass tube. The reaction tube was then pumped free of air, sealed and heated at 35° for 48 hr. During this heating period a white solid precipitated from this solution. The tube was cooled, opened and its contents filtered to yield 1.0 g. of white solid whose infrared spectrum was almost identical to the spectra of the model compound prepared from perfluorobutyrhydrazide and perfluorosebaconitrile before ring closure was accomplished.

The filtrate was diluted with 100 ml. of cold water and 3.5 g. of additional white solid was obtained. This solid gave an infrared spectrum very similar to that of the dimethylformamide-insoluble portion of the product with the exception that it indicated the presence of some cyclic N-H.

c. Perfluorosebaconitrile, 6.2895 g. (0.0139 moles), perfluoroglutarhydrazide, 3.7252 g. (0.0139 moles), and 30 ml. of dimethylformamide were placed in a heavy-wall glass tube. The tube was pumped free of air, sealed and heated at 60° for 12 hr. During this heating period a white solid precipitated from the solution and the temperature was raised to 110° (the temperature required to dissolve the solid in the tube)and maintained at this temperature for four days. The tube was then cooled, opened, and the dimethylformamide solution added to 200 ml. of dry benzene. A very tacky cream-colored solid precipitated from the solution; after drying overnight this product became brittle. This polymer darkened when heated between 260 and 330° but did not melt.

d. Dehydration of the intermediate polymer

Dehydration of the intermediate polymer was carried out by heating the polymer alone under reduced pressure and also by heating in the presence of organic acids.

The intermediate polymer, 1.0 g., was placed in a test tube and heated at 200° for 8 hr. under reduced pressure. During this heating period the solid material darkened but did not melt.

In another dehydration reaction the intermediate polymer, 2.0 g. and 25 ml. of glacial acetic acid were placed in a single-necked, round-bottom flask which was fitted with a water-cooled condenser. The solution was refluxed for three days and during this period a white solid precipitated. Filtration yielded 1.5 g. of white solid polymer; the filtrate was added to 100 ml. of cold water but no additional solids precipitated.

In a third procedure the intermediate polymer, 2.0 g. and 15 ml. of perfluorobutyric acid were placed in a round-bottom flask which was fitted with a water-cooled condenser. The mixture was refluxed for three days but the polymer did not go into solution. The flask was then cooled and the contents filtered to yield 1.7 g. of white solid. The filtrate was added to 200 ml. of cold water but no additional solid precipitated.

7. Polymerization of perfluorosebachydrazide with perfluorosebaconitrile

a. Preparation of methyl perfluorosebacate

Crude perfluorosebacic acid, 25 g., was dissolved in 200 ml. of ethyl ether and filtered in order to remove all insoluble materials. The ether solution was added dropwise to a stirring solution of diazomethane in ether at 0°. After the addition of

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acid was completed, the resulting solution was refluxed for two hr., then the major portion of the ether was removed by distillation. The distillate was colorless indicating that all the diazomethane had reacted. The remaining ether was removed under reduced pressure and the ester, 16.8 g. (63.2% yield) was collected between 90 and 110° under 0.2 mm. pressure.

b. Preparation of perfluorosebachydrazide

Anhydrous hydrazine, 1.28 g., 0.4 moles, dissolved in 30 ml. of methanol, was placed in a two-neck, round-bottom flask which was fitted with a dropping funnel containing 5.18 g., .01 moles, of methyl perfluorosebacate in 15 ml. of methanol. The second neck of the flask was fitted with a pressure equalizing tube which was connected to the top of the dropping funnel. The methyl perfluorosebacate was added dropwise to the stirring solution of hydrazine at room temperature. As the addition proceeded a white solid precipitated from the solution. After the addition of the ester was completed, the white slurry was stirred for one-half hr., cooled in ice water, and filtered. The white solid was washed twice with ice-cold methanol and dried. Obtained from the reaction was 5.0 g. (80% yield) of perfluorosebachydrazide, m.p. 201.5-202°. When the product was recrystallized from a methanol-isopropyl ether mixture, the m.p. was 199-202° and the solid was very pale yellow. The same lowering of the melting point and discoloration was obtained when the product was sublimed.

c. Reaction of perfluorosebaconitrile and perfluorosebachydrazide in dimethyl formamide

Perfluorosebaconitrile, 2.8678 g., .0063 moles, perfluorosebachydrazide, 3.2841 g., .0063 moles, and 60 ml. of DMF were placed in a heavy-wall glass tube. The tube was pumped free of air, sealed, and heated at 45°. After about three hr. of heating at 45°, a white solid began to precipitate from the solution. After 4 days heating, the tube was cooled, opened, and its contents filtered. Obtained from the filtration was 2.4 g. of DMF-insoluble white solid. The filtrate was added to 200 ml. of benzene and 3.3 g. of additional white solid precipitated from the solution. The infrared spectra of both solids were the same and very similar to the spectra of the model intermediate compound. The polymers melted at 265-275° with decomposition.

Dehydration of intermediate polymers was carried out by placing samples of each in single-necked, round-bottom flasks, each fitted with a water cooled condenser; 1.8 g. of DMF insoluble and 2.8 g. of DMF soluble intermediate polymer, were mixed with 50 ml. of glacial acetic acid. The solutions were refluxed for four days, then cooled and added to 200 ml. of benzene. Both precipitates obtained were cream colored and gave infrared spectra which showed that the triazole structure was present.

DMF sol. sample		DMF insol. sample	
yield	2.2 g.	yield	1.4 g.
m.p.	265-275°(dec.)	m.p.	260-275°
m.w.	2440	m.w.	2500

d. Reaction of perfluorosebaconitrile and perfluoro-
    sebachydrazide in dimethyl sulfoxide

Perfluorosebaconitrile, 2.4802 g., .0055 moles, perfluorosebachydrazide, 2.8436 g. .0055 moles, and 55 ml. of DMSO were placed in a heavy-wall, glass tube. The tube was pumped free of air, sealed, and heated at 80° for six days. During this heating period a white solid precipitated from the solution. The tube was further heated at 100° for four days but the precipitate did not dissolve. The tube was cooled, opened, and its contents filtered. A white solid, 4.0 g., insoluble in DMSO at room temperature was obtained. The filtrate was added to 200 ml. of cold benzene but no solids precipitated from the solution. The infrared spectra of this polymer showed that it contained the triazole structure.

The polymer obtained from perfluorosebachydrazide and perfluorosebaconitrile in DMSO, 3.8 g., and 50 ml. of glacial acetic acid were placed in a single-neck, round-bottom flask which was fitted with a water-cooled condenser. The contents of the flask were refluxed for two days and then the insoluble material was removed by filtration. A white solid, 3.2 g., m.p. 265-275°, was obtained. This treatment did not alter the infrared spectra.

8. Treatment of end-groups of poly(perfluoroalkylene-
    1,2,4,4H-triazoles)

a. Poly(perfluoroalkylene-1,2,4,4H-triazole) obtained in the dehydration reactions of the perfluorosebaconitrile-perfluoroglutarhydrazide addition product, 1.0 g., and 50 ml. of 10% sodium hydroxide solution were placed in a round-bottom flask fitted with a water-cooled condenser. The basic solution was refluxed for three days then cooled and a 5 ml. sample of this solution was neutralized with hydrochloric acid. No solid precipitated at the neutralization point but when sufficient hydrochloric acid was added to make the solution strongly acidic, a white solid product precipitated. This solid was isolated by filtration and dried. The product obtained from the sodium hydroxide treatment of the polymer was mixed with a 100 ml. of ethylene glycol and placed in a flask fitted with a water-cooled condenser. The mixture was refluxed for two days during which time the solid dissolved partially to give a cloudy solution. The reaction flask was cooled and 0.2 g. of white solid removed from the solution by filtration. The volume of the filtrate was reduced to 25 ml. by evaporation and the remaining solution was

added to 100 ml. of cold water. No additional solid precipitated from the neutral solution but after acidifying the solution with hydrochloric acid an additional 0.5 g. of white polymer was obtained.

b. The polytriazole prepared from the reaction of perfluoro-sebacohydrazide and perfluorosebaconitrile in DMF, 2.6 g. and 40 ml. of 10% NaOH solution were placed in a flask which was fitted with a water-cooled condenser. The basic solution containing the insoluble polymer was refluxed for two and one-half days. During this heating period the polymer became very tacky but did not dissolve. The flask was cooled and its contents filtered. The insoluble amber solid, 2.4 g., obtained from the filtration was dried by heating at 110° for two hr. under reduced pressure. The infrared spectra of this material contained, in addition to the peaks attributed to the triazole structure, a strong peak at 5.9μ, but no peak for -OH between 2.6 and 3.1μ.

The polytriazole sodium salt, 1.8 g., and 50 ml. of ethylene glycol were placed in a flask which was fitted with a water-cooled condenser. The contents of the flask were refluxed for two days during which the polymer became very tacky but did not dissolve. The flask was cooled and its contents filtered. The very tacky amber solid obtained was dissolved in THF, dried by removing the THF under reduced pressure, and then heating to 230° for 2 hr. The polymer darkened but remained very tacky. The tacky polymer was placed in 25 ml. of aqueous HCl and heated on a water bath for 6 hr. The tacky polymer recovered from the aqueous HCl was then heated at 260° for 2 hr. under reduced pressure. During this heating period the polymer darkened and became very brittle. This brittle material did not dissolve but did swell to several times its original size after standing in THF for 16 hr.

c. The polytriazole prepared in DMSO, 3.0 g., and 50 ml. of 10% NaOH solution were placed in a flask which was fitted with a water-cooled condenser. The basic solution, containing the insoluble polymer, was refluxed for two days, during which the polymer remained insoluble. The flask was cooled and its contents filtered. The cream-colored polymer, 2.8 g., was dried and heated at 110° for 2 hr. under reduced pressure.

The polytriazole sodium salt, 2.8 g., and 50 ml. of ethylene glycol were placed in a flask which was fitted with a water-cooled condenser. The contents of the flask were refluxed for 24 hr. during which the polymer dissolved. The flask was cooled and its contents added to 100 ml. of aqueous HCl. A white precipitate, 2.2 g., was obtained by filtering the aqueous solution. The polymer was dried by heating at 120° for 2 hr. under reduced pressure, m.p. 265-275°, m.w. 4400.

9. Reaction of triazole model compounds with sodium hydroxide

    a. Reaction of 3-perfluoropropyl-5-perfluoroethyl-1,2,4-triazole with NaOH

        To the triazole, 0.25 g., warmed in a water bath, was added dropwise .996N NaOH until the resulting solution was neutral to litmus paper. The solution was evaporated to dryness under reduced pressure and the residue was a pale white solid which was very hydroscopic. This solid was then heated at 250° for 1 hr. under reduced pressure. During this heating period a yellow very tacky material sublimed on the upper walls of the tube and the residue turned brown. The infrared spectra of the sublimate was entirely different from the spectra of the original product. The infrared spectra of the residue did not absorb between 2.5 and 8.0μ.

    b. Heating of 1,3-bis(perfluoropropyl-1,2,4-triazolyl) perfluorooctane with aqueous NaOH

        The bis-triazole, 0.15 g., and 15 ml. of 10% NaOH were placed in a single-neck, round-bottom flask which was fitted with a water-cooled condenser. The resulting solution was refluxed for 2 hr., cooled, and evaporated to dryness under reduced pressure. A pale white residue, m.p. 290-310°, was obtained. The original bis-triazole was obtained by warming this residue in aqueous HCl.

B. Poly(perfluoroalkylene-1,3,4-oxadiazoles)

    1. Revised procedure for preparation of 1,3-bis(tetrazolyl)-perfluoropropane

        Although preparation of 1,3-bis(5-tetrazolyl)perfluoropropane has been described previously,[2] the revised procedure described below has now been adopted as being more convenient and satisfactory.

        Perfluoroglutaronitrile, 75 g. (0.37 moles) was dissolved in 50 ml. of acetonitrile, previously dried by distillation from barium oxide, and added dropwise to a solution of 52 g. (0.8 moles) of sodium azide, 25 ml. of glacial acetic acid and 450 ml. of acetonitrile. The solution was maintained at 5° over the addition period of 1/2 hr. The reaction mixture was allowed to warm to room temperature and, as solids began to appear, the solution was heated to 80° for 20 min. then cooled to room temperature and 35 ml. of concentrated hydrochloric acid added. A voluminous white precipitate appeared upon addition of the acid. An additional 20 ml. of concentrated hydrochloric acid and 100 ml. of acetone were added, the solids removed from the mixture by filtration and the solvents removed under reduced pressure. The solid residue was redissolved in 100 ml. of acetone and again filtered. Removal of the solvent acetone under reduced pressure gave 108 g. of crude

ditetrazole, which was recrystallized from perfluorobutyric acid three times to yield 85 g. of 1,3-bis(5-tetrazolyl)perfluoropropane, m.p. 160.0-160.5°.

2.   Preparation of bitetrazole

This preparation was carried out by modification of the procedure reported by Friederick.[a]

Into a 2 liter three-neck flask fitted with thermometer, mechanical stirrer, and reflux condenser were placed 600 g. of distilled water, 65 g. of sodium azide, 50 g. of sodium cyanide and 55 g. of manganese dioxide. The mixture was cooled to 10° and a solution of 100 g. of sulfuric acid, 80 g. of acetic acid, 200 g. of water and 2 g. of cupric sulfate was added over a period of 1 hr. After addition was complete the solution temperature was raised to 95° over a 4 hr. period and maintained at this temperature for a total of 15 hr. heating. The reaction solution was filtered to remove excess manganese dioxide and the manganese salt of bitetrazole. The solid mixture was washed with 200 ml. of distilled water and then poured into a boiling solution of 56 g. of sodium carbonate in 150 ml. of water and boiled with stirring for 20 min. Insoluble material was removed by filtration and the filtrate decolorized with activated charcoal. The solution was refiltered allowed to cool, whereupon 70 g. of sodium bitetrazole crystallized as a hydrate. Further concentration of the solution gave another 10 g. of the salt or a final yield of 80% of sodium bitetrazole hydrate.

An initial attempt was made to generate free bitetrazole from its sodium salt by dissolving 5 g. of sodium bitetrazole in 25 ml. of water, adding 25 ml. of ethanol slowly and adding nitric acid until the solution was acidic. Mild cooling of the solution induced precipitation of a fluffy white solid which was dried under vacuum. This product detonated at 310°; the reported melting point bitetrazole is 256°. The infrared spectrum of the product isolated showed both the bands characteristic of a free tetrazole group and also those of a tetrazole anion. This product could be converted to bitetrazole by dissolving it in hot perfluorobutyric acid and recovering the bitetrazole on cooling. It could also be converted to the silver salt of bitetrazole. The compound initially isolated in this experiment appears, therefore, to be the mono sodium salt of bitetrazole.

Sodium bitetrazole was successfully converted to the free tetrazole by dissolving 50 g. of the salt in 500 ml. of water and adding excess mercuric nitrate solution slowly. The resulting white precipitate was filtered and washed thoroughly with water then slurried in 700 ml. of water and hydrogen sulfide bubbled through with stirring. Black mercuric sulfide settled out rapidly and after 15 min. the solution was filtered free of the mercuric sulfide and concentrated it to 400 ml. Upon cooling this solution to 0°, bitetrazole, 10 g. (m.p. 258-260°) precipitated.

Further concentration of the solution yielded an addition 5 g. of bitetrazole, m.p. 254-256°. The combined yields were recrystallized from water three times to give 12 g. of bitetrazole, m.p. 258°, yield 35%.

3. Preparation of anhydrous acetic acid

a. Preparation of triacetyl borate

Boric acid, 50.0 g. (0.0801 moles) was mixed with 250 g. (2.45 moles) of acetic anhydride in a 1 liter flask and heated to 60°, whereupon a vigorously exothermic reaction began. The flask was periodically cooled in an ice bath to maintain the temperature below 70°. After 15 min. the reaction subsided and a small amount of solid material was removed by filtration. Upon cooling the reaction solution, white crystals precipitated and were rapidly removed by filtration, then washed with ether and freed of solvent by placing under reduced pressure for 1 day. Total yield of triacetyl borate was 90 g. (50%) m.p. 149-158°.

b. Preparation of anhydrous acetic acid

Reagent grade glacial acetic acid (99.5% assay), 2.1 was fractionated in a glass helices-packed column and the initial cut, b.p. 25-117°, 25 ml., was discarded. Potassium permanganate, 60 g., was then added to the distillation pot and the mixture refluxed overnight. Fractionation was then continued and yielded an additional 200 ml. boiling below 118°. Approximately 1500 ml. of acetic acid, b.p. 118.0° was collected and placed in a tightly stoppered flask. Triacetyl borate, 90 g., was added to the acetic acid and the acid redistilled to give 1200 ml. of anhydrous acetic acid, b.p. 118.0°.

4. Reaction of perfluoroglutaryl chloride with 1,3-bis-(5-tetrazolyl)perfluoropropane

The initial attempts at formation of a poly(perfluoroalkylene-1,3,4-oxadiazole) by this method have been reported previously;[4] these previous experiments were carried out using xylene and diisobutylketone as solvents.

Polymerization using xylene as a solvent was carried out again during the present period by placing 9.5579 g. (3.317×10^{-2} moles) of 1,3-bis(5-tetrazolyl)perfluoropropane in a 300 ml. flask with 125 ml. of xylene previously dried by distillation from barium oxide. The reaction flask was fitted with a reflux condenser, thermometer well and a barostatic dropping funnel. Perfluoroglutaryl chloride, 9.1867 g. (3.317×10^{-2} moles) was placed in the dropping funnel. All of these operations were carried out under an atmosphere of dry nitrogen. The tetrazole solution was stirred with a magnetic stirring bar, heated to 120° and the perfluoroglutaryl chloride added slowly over a period of

2 1/2 hr. The reaction mixture was then heated to reflux and maintained at this temperature for 20 hr. During this period a tan solid precipitated from the solution and adhered to the walls of the flask. At the end of the reflux period the hot xylene was decanted and the remaining solid material rinsed with xylene and dried under reduced pressure to give 8.0 g. of crude polymer melting at 130-180°.

An attempt to cast a film of this crude product from hot acetonitrile resulted only in the deposition of a powder on the sodium chloride plate. However, when this plate was heated for 1 hr. by an infrared lamp, a yellow-brown, transparent film resulted whose infrared spectra showed typical absorption peaks of the perfluoroalkyl-substituted oxadiazole and only a small absorption peak characteristic of the carbonyl group.

A portion of the crude polymer was heated under vacuum at 160° for 1 hr. and became much darker in color. This heated polymer was dissolved in hot acetonitrile and the solution allowed to cool to room temperature, at which point it appeared to form a gel. After standing for five days the acetonitrile solvent had completely evaporated and the polymer remained in the container in two layers, of which the top layer was in light brown and the bottom layer dark brown. The light colored portion was dissolved in tetrahydrofuran and a molecular weight determination (VPO) gave a value of 6800; this product had an m.p. of 165-230°. The bottom layer of polymer was dissolved in tetrahydrofuran and reprecipitated by the addition of water as a light tan solid. Molecular weight of this product was 3220 and it had an m.p. of 140-200°.

The reaction of perfluoroglutaryl chloride with 1,3-bis(5-tetrazolyl)perfluoropropane was also attempted in diethylene-glycol dimethyl ether (diglyme). 1,3-bis(5-Tetrazolyl)-perfluoropropane, 21.1560 g. (7.342×10^{-2} moles) was placed in a dry box in a 200 ml. beaker. Diglyme, which had been dried by distillation from barium oxide at 75° (22 mm. Hg.) and then from lithium aluminum hydride at 75° (22 mm. Hg.), 40 ml., was added to dissolve the tetrazole and the solution poured into a 100 ml. three-neck flask. Perfluoroglutaryl chloride, 20.3360 g. (7.3425×10^{-10} mole) was poured into the beaker and 20 ml. of diglyme added. This solution was added to the flask and the beaker was rinsed with three 10 ml. portions of diglyme. The reaction flask was then stoppered and removed from the dry box and fitted with a reflux condenser which had been flushed with dry nitrogen. Temperature of the reaction mixture was raised to 105° over a period of 40 min. At this temperature a gas was evolved slowly but ceased after 2 hr.; temperature was then raised to 135° and maintained at this point for 18 hr. An infrared spectrum of a small sample of the material at this stage showed the absorption typical of the tetrazole ring, the carbonyl group, and a band at 6.10μ, but not the typical oxadiazole ring absorptions. Continued heating at 135° did not change the appearance of the infrared

spectrum. A solution of 1.0 g. of perfluoroglutaryl chloride in 10 ml. of diglyme was then added slowly to the reaction mixture. An infrared spectrum after this procedure showed that the tetrazole band at 6.85μ had disappeared almost completely but that the carbonyl bands shifted from 5.55μ to 5.6-5.65μ, indicating either hydrolysis or ester formation.

Heating of this reaction mixture was continued for 15 hr. and then the dark-brown solution was poured into 200 ml. of distilled water and a dark-brown oil separated. This oily product was washed by shaking with small quantities of water and then placed in 200 ml. of benzene, in which approximately 75% of the oil dissolved. The remaining 25% was separated and dissolved in tetrahydrofuran. Attempts at precipitation of a solid polymer by addition of water to the tetrahydrofuran solution resulted only in the separation of an oil.

Each of the polymer fractions prepared by carrying out the polymerization reaction in diglyme was acetone soluble, whereas the polymer prepared in xylene was acetone and benzene insoluble.

The reaction of 1,3-bis(5-tetrazolyl)perfluoropropane with perfluoroglutarylchloride was also attempted using acetic acid as a solvent. 1,3-bis(5-Tetrazolyl)perfluoropropane, 10.3907 g. (3.606×10^{-6} mole) was dissolved in 60 ml. of anhydrous acetic acid in a 100 ml. flask fitted with a reflux condenser, a thermometer, and a barostatic dropping funnel. Perfluoroglutaryl chloride, 9.9874 g. (3.606×10^{-2} mole) in 25 ml. of anhydrous acetic acid was placed in the dropping funnel. The reaction solution was heated to 90° and the acid chloride added over a 1 hr. period. The temperature of the reaction was maintained at 90° for 1 hr. and then raised to reflux temperature (119°) for 3 days.

To 10 ml. of the reaction solution was added 50 ml. of water and, after vigorous shaking of the mixture, 0.20 g. of oil separated. Since 2.1 g. of polymer, if water insoluble, should have precipitated from this volume of the reaction mixture apparently 90% of the product was water soluble. A 10 ml. portion of solution was added to 25 ml. of ethyl ether but no separate phase was obtained. The remaining 65 ml. of solution was diluted with water and the aqueous layer decanted from the oily residue that separated. The residue was redissolved in 5 ml. of tetrahydrofuran and a film made of this product on a sodium chloride plate. The infrared spectrum of this material showed strong C=O absorption but no absorption characteristic of the 1,3,4-oxadiazole ring. Tetrahydrofuran solvent was removed and the residue heated under reduced pressure at 125° for 5 hr.; a film cast from the treated product still showed strong C=O but no characteristic oxadiazole absorption in its infrared spectrum.

5. Reaction of perfluoroglutarhydrazide with perfluoro-
   glutaryl chloride

      The perfluoroglutarhydrazide used in this polymeriza-
tion was purified by dissolving 50 g. of the material in 250 ml.
of boiling methyl alcohol and filtering the solution. To this
solution was added 100 ml. of isopropyl ether and the mixture
was cooled to room temperature. A white precipitate was formed
and was filtered and washed with isopropyl ether, then dried for
3 days at 65° under reduced pressure. Yield of purified perfluoro-
glutarhydrazide was 45 g. (90%) m.p. 168-169°.

      Perfluoroglutarhydrazide, 7.1435 g. (2.664×10^{-2} moles)
was placed in a two-neck 250 ml. flask fitted with a reflux
condenser and a barostatic dropping funnel. Anhydrous acetic
acid, 75 ml., was added to the flask. Perfluoroglutaryl chloride,
7.3783 g. (2.664×10^{-2} moles) in 25 ml. of acetic acid was placed
in the dropping funnel. The reaction system was opened to the
atmosphere and protected from moisture by Dry Ice-cooled trap.
The perfluoroglutaryl chloride solution was added at 25° over a
65 min. period. During this time a white solid appeared in the
reaction mixture and the reaction temperature was raised gradually
to the reflux point (116°). When the temperature reached 60°,
the white solid disappeared. The reaction mixture was refluxed
for 1 day and then the bulk of the acetic acid removed by distilla-
tion under reduced pressure to leave a viscous, clear, oily
product.

      This oil, 12.0 g., was heated at 145° for 6 hr. under
reduced pressure. A portion of the material at this stage was
tested and found to be soluble in water, tetrahydrofuran, and
acetone but insoluble in ether and benzene. The infrared spectrum
showed C=O absorption at 5.7μ and also absorption maxima at 6.04
and 6.55μ (weak). This material is a very viscous liquid at 25°.

      Polymerization of perfluoroglutarhydrazide with
perfluoroglutaryl chloride was carried out also using p-dioxane
as a solvent. Into a 100 ml. two-neck flask fitted with a Dry Ice
cooled reflux condenser and a barostatic addition funnel was placed
6.9075 g. (2.576×10^{-2} moles) of perfluoroglutarhydrazide. The
reaction system was swept with dry nitrogen for 15 min. and then
50 ml. of anhydrous p-dioxane was introduced into the flask.
Perfluoroglutaryl chloride, 7.1372 g. (2.577×10^{-2} moles) in 20 ml.
of p-dioxane was placed in the addition funnel and added to the
reaction flask over a 5 min. period with vigorous stirring. At
this point a viscous white paste was formed. The heterogeneous
mixture was stirred at room temperature for 4 hr. during which
time no hydrogen chloride was evolved. Temperature of the reaction
mixture then slowly raised to 85° whereupon hydrogen chloride was
released. The reaction mixture was then raised to 101° (reflux)
over a 1 hr. period and this temperature maintained for 4 hr.
Gas evolution had ceased after this period and the dioxane was
removed under reduced pressure to leave a pale yellow gum. This

gum was placed under reduced pressure for 24 hr. at 120° to remove the last traces of solvent. There remained 11.42 g. of poly-(perfluoroalkylenediacylhydrazine), yield 94%, m.p. 300°.

The molecular weight (VPO) of the crude polymer in tetrahydrofuran was 1855. The infrared spectrum in dioxane showed N-H stretching at 3.13-3.14μ, C=O doublet at 5.66 and 5.78μ and N-H deformation at 6.60μ. The polymer was soluble in acetone, ethyl alcohol, dioxane and tetrahydrofuran and insoluble in acetonitrile, acetic acid, water, nitric acid, polyphosphoric acid, benzene and ethyl ether.

A later polymerization of perfluoroglutaryl chloride with perfluoroglutarhydrazide was carried out in apparatus constructed particularly to prevent moisture entering the reaction system. The system was flamed and swept with dry nitrogen several times to eliminate all traces of moisture. Perfluoroglutar-hydrazide, 10.8636 g. (0.04051 moles) was added to the reaction flask and perfluoroglutaryl chloride, 11.2205 g. (0.04051 moles) was placed in the barostatic funnel. Dioxane was distilled from sodium directly into the addition flask and the system was swept with dry nitrogen. Approximately 75 ml. of dioxane was then allowed to run into the flask holding the hydrazide and stirring was started. 25 ml. of dioxane was added to the acid chloride and the acid chloride solution was then added dropwise to the hydrazide and stirred overnight at room temperature. Heating was started and hydrogen chloride was observed to evolve at about 70°. The temperature was then raised to the reflux point (101°) at which point all solid material had gone into solution. The evolution of hydrogen chloride continued for a period of 20 days. At the end of this time the dioxane was removed under reduced pressure to leave a very viscous amber polymer. Heating this polymer for four days at 160° left a light brown powder which was soluble in acetone, tetrahydrofuran, methanol and dimethylsulfoxide.

Several fractions of polymer were recovered from a 1 g. sample using methanol as a solvent and precipitating the polymer fractions by the addition of water. The first fraction melted with decomposition at 290° and had a molecular weight of 3700 (VPO). This represents a degree of polymerization of about 16. Two other fractions melted at 285° with decomposition. The last fraction melted at 285° and had a molecular weight of 3400. From this procedure approximately 8-10 g. of polymer in the 3400-3700 molecular weight range was recovered for subsequent ring closure studies.

6. <u>Reaction of perfluoroglutarhydrazide with perfluoroadipoyl chloride</u>

Perfluoroglutarhydrazide, 7.4894 g. (2.793x10^{-3} mole) was allowed to react with perfluoroadipoyl chloride, 9.1338 g. (2.793x10^{-3}) in the manner described above for the reaction of perfluoroglutaryl chloride. After removal of the solvent acetic

acid the polymer product (gum) was heated at 140° for 24 hr. under
reduced pressure. Infrared analysis (film from tetrahydrofuran)
showed C=O absorption at 5.72μ, a maximum at 6.06μ and a weak
maximum at 6.5μ. At room temperature this product is a glass.
Molecular weights have not yet been determined.

7. Attempted dehydration of the poly(perfluoroalkylene-
   diacyl-hydrazine)

1.2155 g. of poly(perfluoroalkylenediacylhydrazine)
was placed in a tube and heated under reduced pressure at 265°
for 2 hr. Weight loss during this time was 0.0795 g. Infrared
analysis of the resulting product in tetrahydrofuran did not
show the characteristic ring absorption of the 1,3,4-oxadiazole
group. The molecular weight (VPO) of the polymer after this
heating procedure was 2950 in tetrahydrofuran.

A further attempt was made to dehydrate the poly-
(perfluoroalkylenediacylhydrazine) by heating 0.1 g. of the polymer
in 20 ml. of dioxane with an excess of phosphorus pentoxide for
3 hr. Infrared analysis of the solution after 1 hr., 2 hr., and
3 hr. heating showed only the absorption bands characteristic of
the starting material and none of those attributed to the
oxadiazole group. A similar reaction was attempted using
tetrahydrofuran with phosphorus pentoxide at reflux temperature
for 24 hr. but no oxadiazole ring formation could be detected
from the infrared spectrum.

IV. REFERENCES

1. ML-TDR-64-142 Pt. II

2. WADC-TR-59-272 Pt. IV

3. Walter Friederick, U S. Pat. 2,710,297, June 7, 1955

4. WADC-TR-59-272 Pt. V

V. APPENDIX

(Infrared Absorption Spectra)

1. Perfluorosebachydrazide

2. N,N'(Perfluorobutyrimidoyl)perfluoroglutarhydrazide

3. N,N'-<u>bis</u>(Perfluorobutyryl)perfluoroglutarhydrazidine

4. 1,8-<u>bis</u>$\left[$5-(3-perfluoropropyl-1,2,4-triazolyl)$\right]$ perfluoro-octane
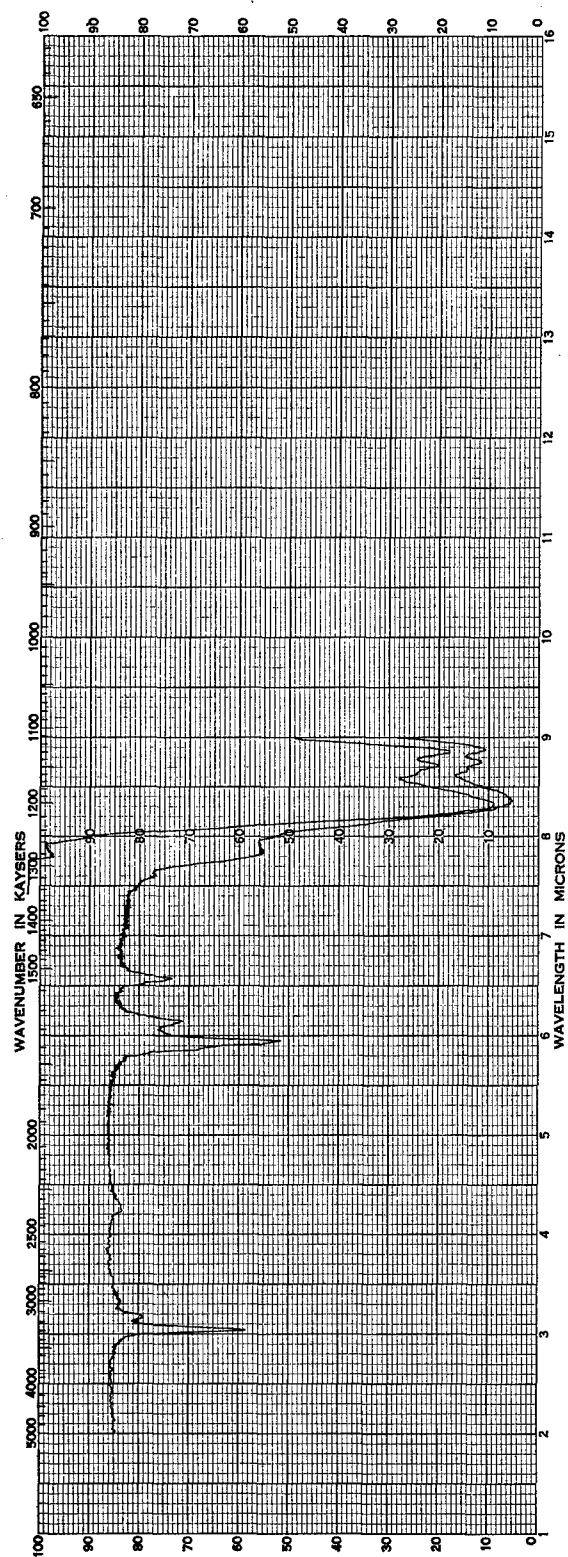
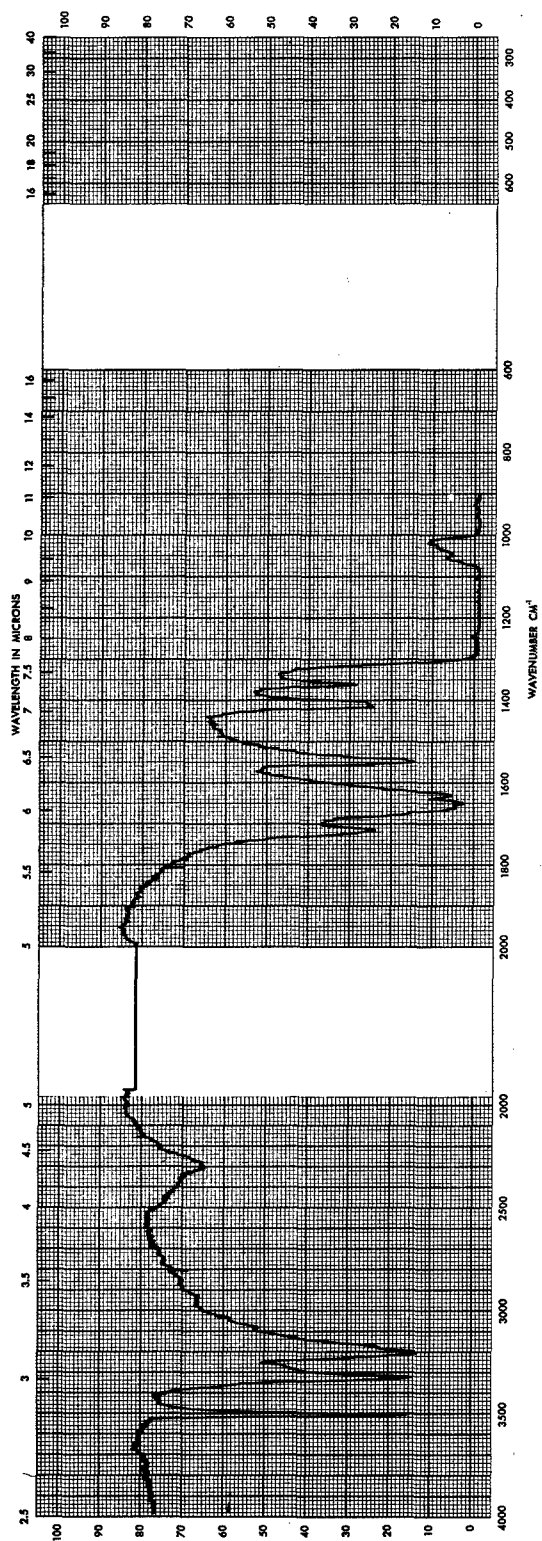5. Poly(perfluorooctene-1,2,4-triazole)

Fig. 1   Perfluorosebachydrazide

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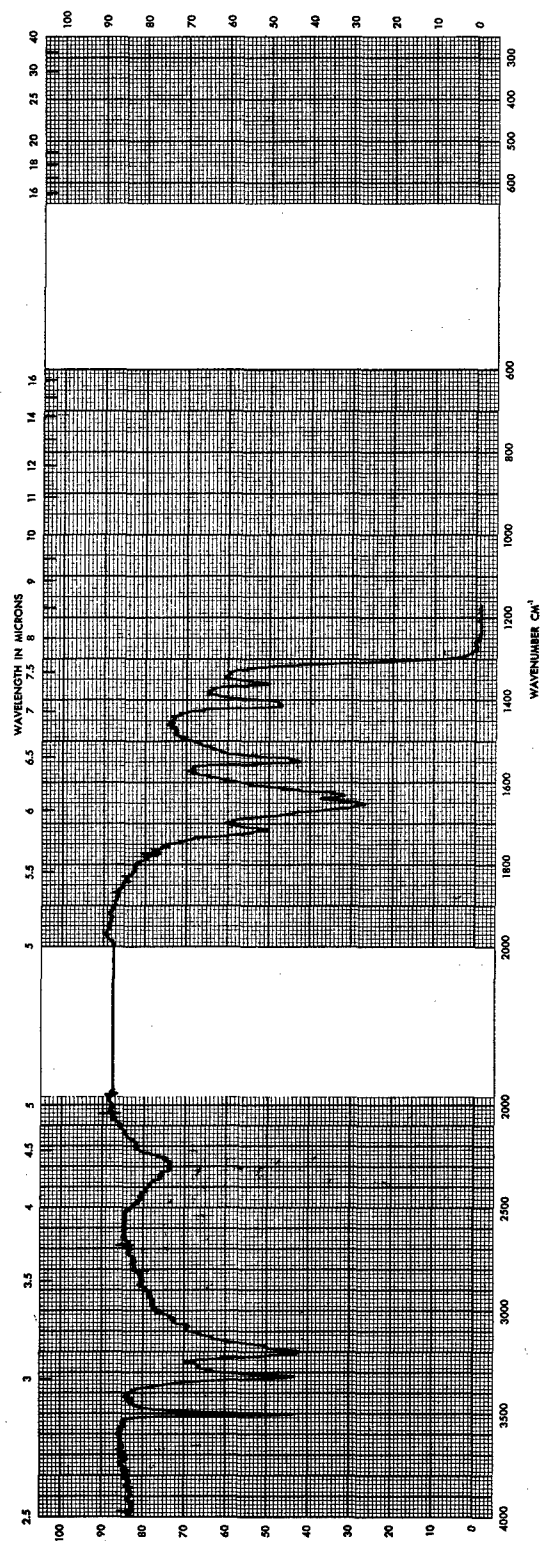Fig. 2 N, N' - bis(Perfluorobutyrimidoyl) perfluoroglutarhydrazide.

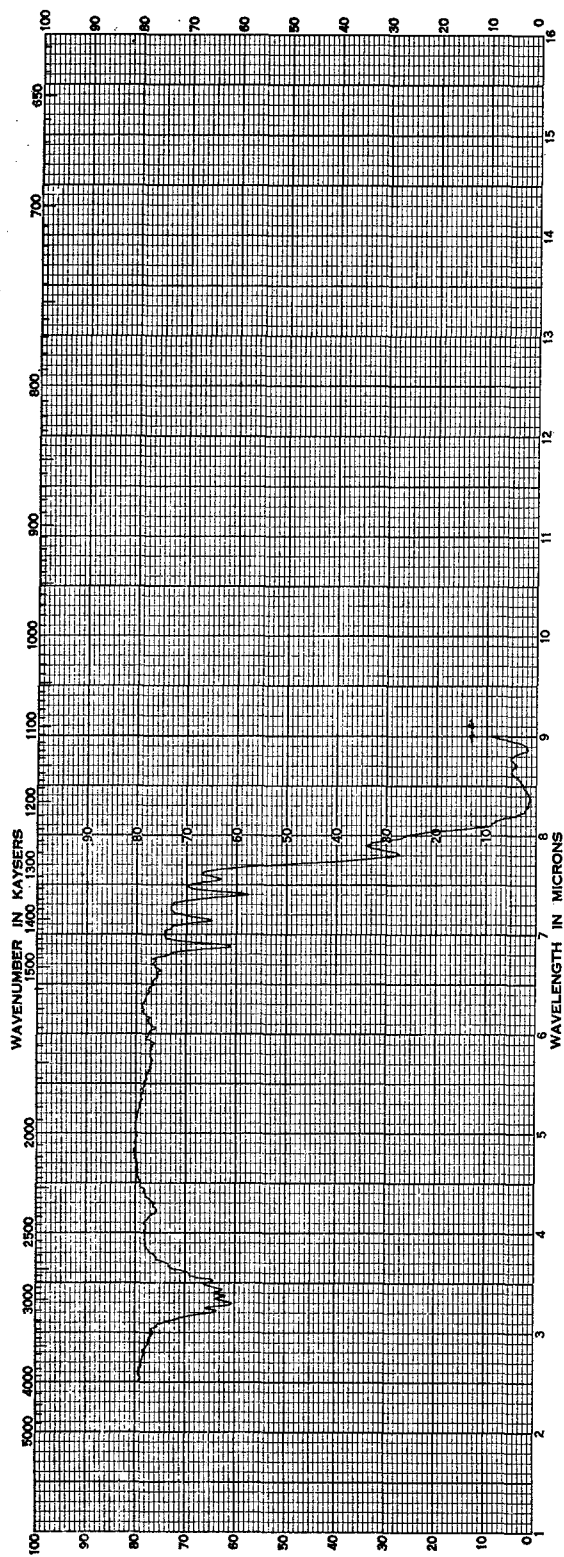Fig. 3 N, N' - bis (Perfluorobutyryl) perfluoroglutarhydrazidine.

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Fig. 4 1, 8 - bis [5-(3-perfluoropropyl 1,2,4-triazolyl)] perfluorooctane

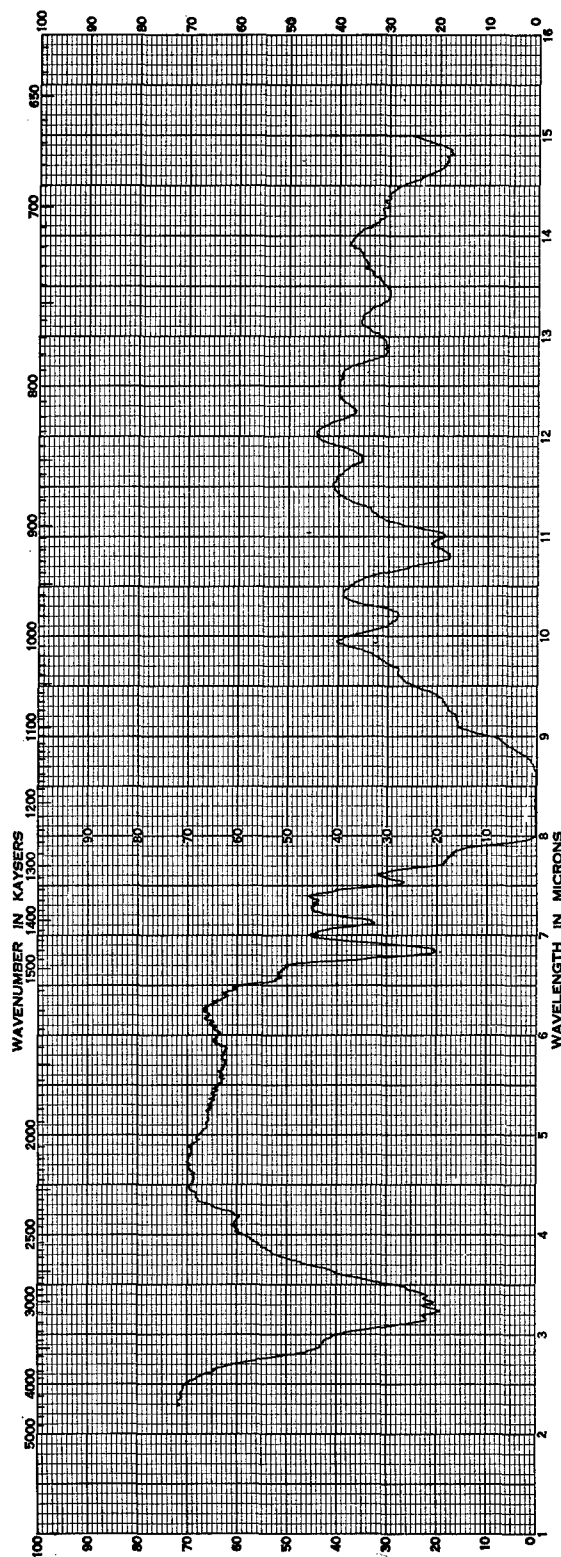Fig. 5 Poly(perfluorooctene 1, 2, 4-triazole)

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Nonmetallic Materials Division, Air Force Materials Laboratory, Research & Technology Div., Air Force Systems Command, W-PAFB,O.

13. ABSTRACT

Work on the poly(perfluoroalkylene-1,2,4,4$\underline{H}$-triazole) system has been continued with the objectives of increasing the polymer molecular weights, inactivating the polymer chain end-groups and studying polymer chemical and physical properties. A new synthesis of an intermediate polymer structure for this system has been found which involves addition of perfluoroalkyl-dihydrazides to perfluoroalkyldinitriles in a highly polar solvent. Inactivation of end-groups has been possible by conversion to $-CF_2COOH$ with subsequent decarboxylation to $-CF_2H$.

Methods of synthesis of poly(perfluoroalkylene-1,3,4-oxadiazoles) that have been studied include the direct formation of the oxadiazole ring by acylation of a bis(tetrazolyl)perfluoroalkane and formation of an intermediate poly(perfluorodiacyl hydrazine) from the reaction of perfluorodiacyl chlorides with perfluoroalkyldihydrazides.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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